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UNIVERSITY OF ALBERTA

THE EFFECT OF CONSERVATION FREEZING TREATMENTS ON SELECTED PROPERTIES OF WOOL

BY
CRYSTAL A. DAWLEY

A Thesis
submitted to the Faculty of Graduate Studies and Research in
partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

DEPARTMENT OF CLOTHING AND TEXTILES

Edmonton, Alberta
SPRING, 1993

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I wish you every success with your thesis.

Yours sincerely

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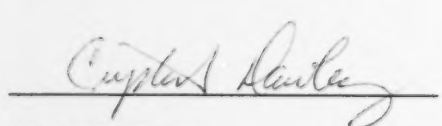

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled THE EFFECT OF CONSERVATION FREEZING TREATMENTS ON SELECTED PROPERTIES OF WOOL submitted by CRYSTAL A. DAWLEY in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in CLOTHING AND TEXTILES.

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DATE: March 29, 1993

ABSTRACT

The freezing of textiles is common in the museum community. Long term freezer storage is used to preserve archaeological textiles. Freezing and thawing is used to kill insects infesting textile artifacts. Outside of museums, textiles in northern archaeological sites may be exposed to seasonal freezing and thawing or be frozen in a permafrost layer for several years. The purpose of this project was to determine if freezing had a damaging effect on wool textiles and if the moisture content of the wool during freezing had an effect on the results.

Dry and wet new wool yarns were sealed in freezer storage bags and frozen at -25°C by one of two methods: repeated 24 hour freeze-thaw cycles and continuous freezing. Before freezing and after 20, 40, and 60 days, the yarns were evaluated for tensile strength, extension at break, energy at break, moisture regain at 11%, 32%, 53%, 65%, 75% and 97% relative humidity, BET monolayer value, tributylphosphine-alcoholic sodium iodide solubility, and SEM appearance. The quantitative results were statistically analyzed using two-way analysis of variance (α=0.05) and multiple comparisons by Duncan's Multiple Range and Scheffé's tests.

The results suggested that after 60 days, neither freezing and thawing nor continuous freezing of dry or wet wool yarns caused significant changes in the properties evaluated. The extension at break and moisture regain at 97% RH suggested that after 60 days of continuous freezing, regardless of the moisture content of the wool, the size or number of intermolecular spaces within the fibres may have increased. The solubility test results did not reveal differences in fibre molecular structure after freezing. The microscopic appearance of the fibres suggest no changes in fibre structure after freezing. There were differences in the tensile strength and extension at break between wool yarns which were dry and those exposed to wet conditions but these differences were not influenced by freezing.

It was concluded that cyclical and continuous freezing at -25°C for up to 60 days have no significant effect on the measured properties of the wool. Whether the wool yarns were dry or wet during freezing had limited effect on the properties which were evaluated.

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CHAPTER 1 INTRODUCTION

Justification and Statement of Purpose

Textiles may be exposed to freezing conditions in a variety of situations. Archaeological textiles *in situ* are often exposed to seasonal freezing and thawing cycles. Textile conservators use freezing and thawing as a method of killing insects. Textiles may also be exposed to continuous freezing. Freezers are used for short- and long-term storage of wet archaeological textiles while awaiting conservation treatment. Archaeological textiles situated in the permafrost layer may be continuously frozen for hundreds of years.

Archaeological textiles in northern regions may be exposed to hundreds of freeze-thaw cycles in undisturbed sites before being excavated and removed to the laboratory for analysis. Once the textiles have reached the laboratory, the conservator must make decisions regarding treatment, storage, and possible display. The actions taken must be appropriate to prevent further damage and to extend the life expectancy of the textile given the condition it is in at that point in time. Kerr and Schweger (1989) expressed a concern that it was difficult to identify whether damage to wool textiles from a northern archaeological site was caused by microorganisms, the effects of freezing and thawing cycles, or a combination of the two. Both factors have been found to create similar damage. The ability to identify the cause of any damage will aid the textile conservator in preventing further damage of the same nature, especially if the damage is due to microorganisms.

The second situation where textiles may be exposed to cyclical freezing and thawing is in the treatment of textiles for insect infestation. Freezing methods have been suggested in order to kill insects which infest and cause damage to artifacts (Brokerhof, 1989; Dodd 1991; Florian, 1986; "To Freeze", 1991). Gilberg & Brokerhof (1991) discuss a freezing method which is highly effective in killing the insects. Although these researchers suggest that the freezing-thawing method will not have a damaging effect on textiles, as yet, there is no documented evidence directly supporting this idea (Brokerhof; Dodd; Florian; "To Freeze").

Short- and long-term freezer storage of water-saturated artifacts from wet archaeological sites is a common method used to prevent degradation (Gardner, 1988; Jakes & Mitchell, 1992; Logan & Newton, 1986). Saturated textiles from underwater or waterlogged sites are sealed in plastic and stored on dry-ice or in a home or commercial freezer, at freezer temperatures near -20 to -25° C, until they may be examined by a conservator (Gardner; Logan & Newton). These artifacts may be frozen for as little as one week or for up to several years.

There is a need to examine the effects of freezing treatments on museum and archaeological textiles. Florian (1986) states: "It is our ethical responsibility as conservators to determine to the best of our ability if freezing treatments are damaging to artifacts". Exposure to freeze-thaw cycles was briefly noted by Howard and McCord (1960) as a cause of physical damage to cotton textiles; however, elaboration beyond this point was not made. It is known that foods exposed to long term freezer storage may become dehydrated through freeze-drying (Boegh-Soerensen & Jul, 1985). Dehydration of textiles exposed to long term freezer storage is a possibility. Jakes and Mitchell (1992) determined that within a few months, textiles frozen while exposed to low relative humidity and a low air current experienced "slow-drying". Commercial freeze-drying procedures have been used in the conservation of archaeological materials; successfully drying the artifacts while preventing structural collapse (Peacock, 1990). The effects of freeze-drying on archaeological textiles are being examined elsewhere (E. Peacock, personal communication, April 6, 1991).

There has been little research carried out to study the effects of freezing on textiles. Jakes and Mitchell (1992) found that linen fabrics which were slow-dried under freezing conditions retained an acceptable appearance. Ito, Sakabe, Miyamoto, and Inagaki (1984), studied the freezing and thawing of wool. The purpose of this research was to completely separate the orthocortex and paracortex of the fibre. The freezing conditions used in this study were severe. Fibrillation of wool fibres was only achieved by freezing and thawing if fibres had the cuticle removed and were treated with formic acid prior to freezing (Ito et al.). It is desirable to determine if less severe freezing conditions will create the same type of damage. If

not, fibrillation of wool fibres found in archaeological contexts may more readily be attributed to microorganisms than to freezing because fibrillation of wool fibres may be caused by some microorganisms (Lewis, 1981, p. 72; Nopitsch, 1953). The temperature and relative humidity of an environment will influence the growth of microorganisms (Lewis; Nopitsch).

Freezing treatments may affect different types of fibres in different ways. In order to limit the scope of this research, the fibre to be studied has been confined to wool. Wool was chosen because it and other hair fibres are more likely to be encountered in frozen archaeological sites than fibres such as cotton or silk. Wool and hair fibres are often used in textile items which are intended to provide the user with insulation from the cold, commonly in colder, northern regions. As well, wool textiles are generally those which are in most danger of attack by insects. The freeze-thaw treatment is recommended particularly for wool artifacts. Clothes moths (*Tineola bisselliella* and *Tinea pellionella*) and carpet beetles (*Attagenus megatoma* and *Anthrenus verbasci*), two types of insect pest commonly found in museum collections, feed on proteins including wool and hair fibres (Story, 1985).

It should be kept in mind that wool is a very absorbent fibre. The moisture content of wool at saturation has been reported as 33-35% (Alexander, Hudson, & Earland, 1963, p. 87; Watt, 1980). Associated with this sorption of water vapor is a swelling of the fibre. During swelling, the sorbed water molecules push the cortical cells and the protein molecules within these cells apart, weakening and possibly breaking some intermolecular crosslinks. As well, there is a volume increase of water in the phase change from liquid to solid ice. If this volume increase is allowed to take place within the wool fibre, further separation of the cortical cells and/or the molecules is possible, depending on the location of the water within the fibre. After prolonged exposures to continuous freezing, the size of ice crystals within a material tends to increase (Boegh-Soerensen & Jul, 1985). Thus, there is a concern that the freezing of wool may cause damage to the fibre. The repeated stress on the fibre as a result of swelling during cyclical freezing and thawing may increase the opportunities for damage to occur.

Problem Statement

The problem to be addressed in this research project is: Do freezing treatments have a damaging effect on wool textiles and does the condition of the wool influence these results? The ability to answer this question depends on whether damage from these conditions can, in fact, be identified or measured.

Objectives

1. To subject new, clean, wool yarns to one of two conditioning treatments prior to freezing:
   a) 65 ± 2% relative humidity, 20 ± 2°C ("dry");
   b) wet-out with distilled water ("wet").

2. To subject new, clean, wool yarns to one of the following freezing treatments:
   a) repeated 24 hour freeze-thaw cycles for a maximum 60 cycles;
   b) continuous freezing for a maximum of 60 days.

3. To study the effects of the conditioning and freezing treatments after 20, 40, and 60 cycle(day) intervals, on the following wool properties: tensile strength, extension, energy to break, moisture regain at six relative humidities ranging from 11% to 97%, BET monolayer value, and tributylphosphine-alcoholic sodium iodide solubility.

4. To observe the appearance of the fibres after 60 cycles(days) of freezing using scanning electron microscopy.

5. To compare the effects of dry condition with wet condition during freezing on the properties of wool fibres.

6. To compare the effects of continuous freezing with cyclical freezing on the properties of wool fibres .

Null Hypotheses

1. There is no significant difference in the tensile strength of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

2. There is no significant difference in the extension at break of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

3. There is no significant difference in the energy to break of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

4. There is no significant difference in the moisture regain at 11% relative humidity of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

5. There is no significant difference in the moisture regain at 32% relative humidity of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

6. There is no significant difference in the moisture regain at 53% relative humidity of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

7. There is no significant difference in the moisture regain at 65% relative humidity of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

8. There is no significant difference in the moisture regain at 75% relative humidity of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

9. There is no significant difference in the moisture regain at 97% relative humidity of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

10. There is no significant difference in the BET monolayer value of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

11. There is no significant difference in the tributylphosphine-alcoholic sodium iodide solubility of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Limitations

1. The results of this experiment will be directly applicable only to the new, clean wool tested.

2. The time frame used for the freezing treatments is a compromise and may produce results which are different from those which may occur under practical conditions.

3. The methods used for the evaluation of the changes in the wool are limited to those for which equipment and supplies were readily available.

Definitions

For the purpose of this study, the following definitions will apply:

Energy at Break: also known as *work of rupture* or *toughness* ; the energy (Joules) needed to break the fibre and is equal to the area under the stress-strain curve. (Morton & Hearle, 1975, p. 269)

Equilibrium Moisture Content: the condition reached by a sample when it no longer takes up moisture from or gives moisture to the surrounding atmosphere. (ASTM D 123-90a, 1990)

Extension at Break: the change in length of a material due to stretching at the breaking point; extension (%) = $100\ \Delta L/L_O$ (ASTM D 123-90a, 1990)

Moisture Regain: the amount of moisture present in a specimen at a constant relative humidity expressed as a percentage of the dry mass of the specimen,

$$R = \frac{\text{initial mass - oven-dry mass of specimen}}{\text{oven-dry mass of specimen}} \times 100\%$$

(CAN/CGSB-4.2 No. 3-M88)

Saturation Moisture Content: the equilibrium moisture content of an item at 100% relative humidity. (Morton & Hearle, 1975, p. 168)

Relative Humidity: a measure of the dampness of air; the ratio of the vapor pressure of water in the atmosphere to that in equilibrium with liquid water at the same temperature and can be expressed as a percentage. (Zeronian, 1984, p. 122)

$RH = h/h_S \times 100\%$:

h = the *absolute humidity* of an atmosphere: the mass of water vapor per unit volume of air

h_S = the absolute humidity of saturated air at the same temperature (Morton & Hearle, 1975, p. 161)

Sorption: the process of taking up or holding a material by *adsorption, absorption* or both. (ASTM D 4920-89)

Absorption: a process in which one material (the absorbent) takes into its spaces, or absorbs, another (the absorbate); as in the absorption of moisture by fibres. (ASTM D 4920-89)

Adsorption: a process in which the surface of a solid takes on, or adsorbs, in an extremely thin layer molecules of gases, of dissolved substances, or of liquids with which it is in contact. (ASTM D 4290-89)

Desorption: a process in which a sorbed material is released from another material, as the desorption of moisture from fibres; the reverse of absorption, adsorption, or both. (ASTM D 4290-89)

Water Activity: the ratio of partial pressure of water in the material to the vapor pressure of pure water at a given temperature, and is equal to the equilibrium relative humidity divided by 100. (Karel, 1975, p. 239-240)

Wet Specimen: a specimen which has been immersed in liquid water. Liquid water is held within spaces between the fibres of a textile material.
vs. *regain moisture* which refers to water molecules (taken in from the atmosphere) held in spaces within the molecular structure. (Merkel, 1991, p. 307)

Wool: the fibre from the fleece of the sheep or lamb. (ASTM D 123-90a)

CHAPTER 2 REVIEW OF THE LITERATURE

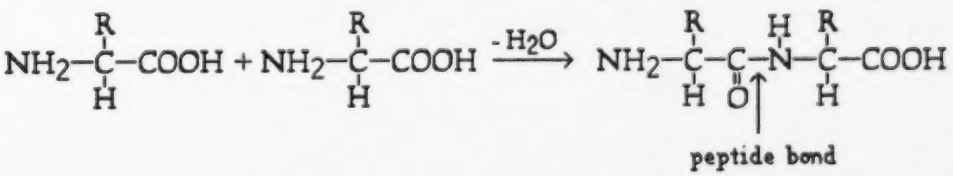
Introduction

In order to evaluate the effects of freezing treatments on wool textiles, it is necessary to have an understanding of the structure of wool and the physical and chemical properties of this protein fibre. The factors contributing to the degradation of wool should also be considered. Characteristics of the wool-water system should be examined and an understanding of freezing theory and ice crystal formation is necessary. The application of freezing treatments in textile conservation should be described. These topics will be addressed in the following literature review.

Wool

Structure of Proteins

Proteins are polymers made up of α-amino acids. The amino group (NH_2) of an amino acid is attached to the α-carbon, the carbon next to the carboxyl group (COOH) of that amino acid. A hydrogen atom and a side chain (R) are attached to the α-carbon of every amino acid (Mathews & van Holde, 1990, p. 133). Peptide bonds between the carboxyl and amino groups of two separate amino acids, formed by a condensation reaction eliminating one molecule of water, covalently link the amino acids to form polypeptides (Equation 1) (Mathews & van Holde, p. 142).



[1]

The peptide bonds are susceptible to hydrolysis by acids, alkalis, enzymes, and treatments with hot water (Alexander, Hudson, & Earland, 1963, p. 288; Maclaren & Milligan, 1981). Most

polypeptides retain an unreacted amino group at the amino or "N-terminus" and an unreacted carboxyl at the carboxyl or "C-terminus".

There are approximately 20 common amino acids found in proteins. It is the unique structure of the side chains on each amino acid that differentiates the individual amino acids. The side chains may be characterized as hydrophobic or hydrophilic, polar or non-polar, or by the presence of ionizable groups (Mathews & van Holde, 1990, p. 137). The size of the side chains plays a role in determining protein structure; for example, bulky side groups, such as that of tyrosine, prevent close packing of molecular chains (Jakes & Howard, 1986).

The three-dimensional structure of proteins is either globular or fibrous. The polypeptide chains of globular proteins are folded into compact structures which suit that protein to a particular role of transportation, synthesis, or metabolization (Mathews & van Holde, 1990, p. 186). An example of a globular protein is the hemoglobin of red blood cells. The more crystalline fibrous proteins generally play structural roles in animal cells and tissues. The fibrous proteins include collagen, an important constituent in skin; fibroin, the protein in silk; elastin, found in arterial blood vessels; and keratin, the protein of horn, hair and wool (Mathews & van Holde, p. 179-184).

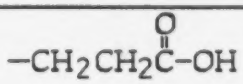
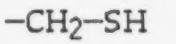
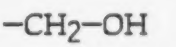
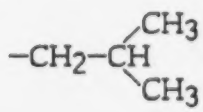
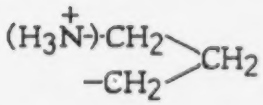
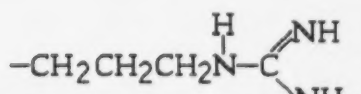
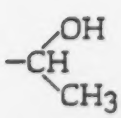
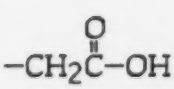
Keratins are fibrous proteins distinguished by the presence of cystine disulphide bridges between neighbouring polypeptide chains (Mathews & van Holde, 1990, p. 181). There are two classes of keratin, α-keratin and β-keratin. Alpha-keratins are helical in structure whereas β-keratins are sheet-like (Mathews & van Holde, p. 181) and sometimes result from the stretching and unfolding of α-keratins.

Chemical Composition of Wool Fibres

Wool is primarily made up of hard α-keratin protein consisting of 18 amino acids (Table 1). The keratins which are classified as hard keratins, such as wool and hair, do not have a consistent amino acid composition. There may be variations in amino acid composition of hair amongst different species, within different animals in the same species or even within

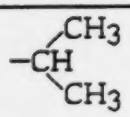
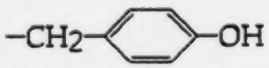
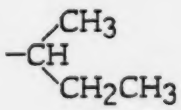
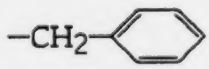
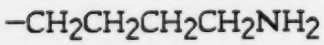
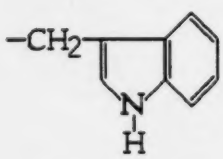
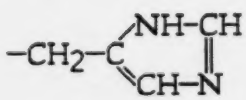
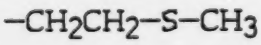
the same animal (Marshall, Orwin, & Gillespie, 1991) Each species, however, does have its own characteristic compositional range.

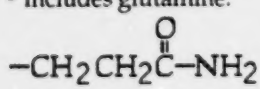
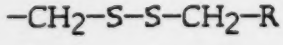
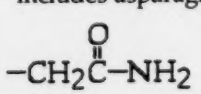
Table 1
Amino Acid Composition of α-Keratin (mole %)

Amino Acid	Mathews & van Holde (1990)	Leeder & Marshall(1982)	Structure of (R) Side Chain[a]	Polar
Glutamic Acid[b]	12.1	11.9		yes
Cysteine[c]	11.2	10.0		when ionized
Serine	10.2	10.5		yes
Glycine	8.1	8.2		
Leucine	7.7	7.7		
Proline	7.5	7.2		
Arginine	7.2	6.9		yes
Threonine	6.5	6.3		yes
Aspartic Acid[d]	6.0	6.6		yes

Continued

Table 1 (Continued)
Amino Acid Composition of α-Keratin (mole %)

Amino Acid	Mathews & van Holde (1990)	Leeder & Marshall(1982)	Structure of (R) Side Chain[a]	Polar
Valine	5.1	5.7		
Alanine	5.0	5.4		
Tyrosine	4.2	3.7		partial
Isoleucine	2.8	3.1		
Phenylalanine	2.5	2.8		
Lysine	2.3	2.8		yes
Tryptophan	1.2	---		
Histidine	0.7	0.8		
Methionine	0.5	0.4		yes
Total	100%	100%		

[a] adapted from Mathews and van Holde (1990, p. 136) and Dusenbury (1963, p. 222-223).
[b] includes glutamine: 
[c] includes cystine: 
[d] includes asparagine: 

Wool is rich in cysteine, serine, glutamic acid, glycine and leucine. The amino acid cysteine is present in relatively large amounts, approximately 12% by weight (Alexander et al., 1963, p. 244; Marshall et al., 1991). Cysteine is noted because of its sulphur content and its ability to form covalent disulphide bonds, also known as cystine links. Most cysteine residues (>95%) are oxidized during keratinization to give cystine crosslinks both within and between protein chains (Marshall et al.). These strong, covalent disulphide bonds are important in determining the structure of the protein and therefore contribute to the stability and many of the chemical characteristics of wool (Maclaren & Milligan, 1981, p. 10). The mechanical strength, elastic properties and chemical and biological resistance of keratins stem from the three dimensional structure stabilized by the strong disulphide bonds (Marshall et al.). If the disulphide bonds are damaged or broken, the structure of wool may be severely altered.

The presence of polar groups contributes to hydrogen bonding which also makes a major contribution to the stabilization of the structure of wool protein (Alexander et al., 1963, p. 288). The main polar groups in proteins are the free amino (NH_2), carboxyl (COOH) and hydroxyl (OH) groups of the amino acid side chains (Leeder & Watt, 1965). Hydrogen bonding occurs between polar groups within the polypeptide chain and between chains, generally between amide (NH) and carbonyl (C=O) groups.

Hydrogen bonding also occurs between the protein and water. Some water molecules reside in the internal structure of the molecule and stabilize the conformation (LeMaguer, 1987). Hydrophilic amino acid residues and peptide groups ensure significant adsorption of water vapor (Watt, 1980). The presence and location of polar groups influences moisture sorption properties by providing binding sites for water molecules.

Ion-ion salt links are another type of intermolecular force contributing to the structure of wool. The electrostatic attraction between acidic (COO^-) and basic (NH_3^+) side groups forms the salt link which influences the strength of the polypeptide (Alexander et al., 1963, p. 180).

Protein constitution of wool.

Keratin protein is actually made up of several (100+) constituent proteins (Marshall et al., 1991). There are generally 3 classes of constituent proteins that have been determined through analysis of keratin extracts. These three classes are referred to as "IF" or "low-sulphur", "high-sulphur", and "high-tyrosine" (Marshall et al.). The two major types of proteins within the cortical cells are the low sulphur and high sulphur proteins. Chapman (1969) identifies these two main protein groups as SCMKA (low sulphur) and SCMKB (high sulphur). The high-tyrosine proteins are located only in the matrix between the intermediate filaments (Marshall et al.). The high-tyrosine proteins are the smallest of the three protein groups with molecular weights less than 10,000 (Marshall et al.).

The SCMKA, proteins are the large helical component of the keratin that comprise the microfibrils or intermediate filaments (IFs). These IF polypeptides are the low-sulphur proteins which are the more crystalline, more ordered protein chains that wind together to form the intermediate filaments. The IF polypeptides are the largest with molecular weights ranging from 45,000 to 58,000 (Woods cited in Marshall et al., 1991). These polypeptides alone contain α-helices and are rich in the amino acids which favour α-helix formation (eg. lysine, aspartic acid, glutamic acid, and leucine) (Marshall et al.). The IF proteins consist of two families of low sulphur polypeptides containing both helical and non-helical segments, of comparable size, charge and amino acid composition.

The high sulphur proteins with high cysteine content are found in the less ordered matrix between the intermediate filaments. The SCMKB proteins are globular in nature and a highly crosslinked network results due to the high cystine content . The major protein family in wool is the SCMKB2A group with a molecular weight of approximately 19,000. According to Marshall et al. (1991), about 85% of the molecule is of the repeating sequence:

-cys-cys-x-pro-y-

where: x= glutamine, glutamic acid, or arginine
y= serine, or threonine.

Physical Structure of Wool Fibres

Wool fibres are morphologically complex and although they have both crystalline and amorphous regions, the fibre is highly amorphous. Wool fibres are generally considered to have three structural components: the cuticle, the cortex, and the cell membrane complex (Figure 1). Many hair fibres have a central core, the medulla; however, the medulla is present generally only in coarse wool and hair fibres (Cook, 1968, p. 99) and will not be discussed in detail.

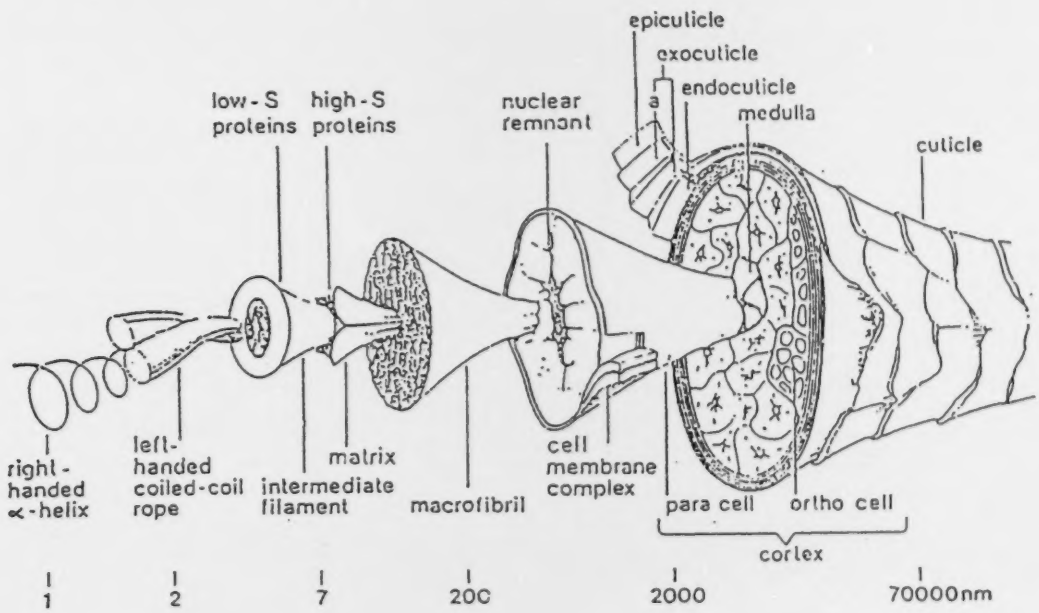


Figure 1: Schematic diagram of a hair fibre

Note. From "Structure and Biochemistry of Mammalian Hard Keratin" by R. C. Marshall, D. F. G. Orwin, and J. M. Gillespie, 1991, Electron Microscopy Review, 4, p. 49. Copyright 1991 by Pergamon Press Ltd.. Reprinted by permission.

The Cuticle

The cuticle is made up of the cuticle cells and the epicuticle layer (Cook, 1968, p. 99). The cuticle comprises no more than 10% of the total weight of the fibre (Watt, 1980). The cuticle cells are the flat, overlapping, scales on the external surface of the fibre which serve to protect the fibre (Cook, p. 99). The cuticle cell layer is one cell thick (Maclaren & Milligan,

1981, p. 2). The main morphological features of the cuticle cells are the sulphur-rich, resistant exocuticle and the less resistant endocuticle (Marshall et al., 1991) (Figure 2). The epicuticle is a thin (3 nm) chemically resistant, semi-permeable membrane which envelopes each cuticle cell (Alexander et al., 1963, p. 9; Cook, p. 99; Marshall et al.). This membrane is the outermost layer of the fibre and it repels liquid water, yet is permeable to water vapor (Cook, p. 99). Diffusion can occur preferentially between, rather than through, the cuticle cells (Leeder, 1986). The cuticle layer is separated from the cortical cells by the cell membrane complex.

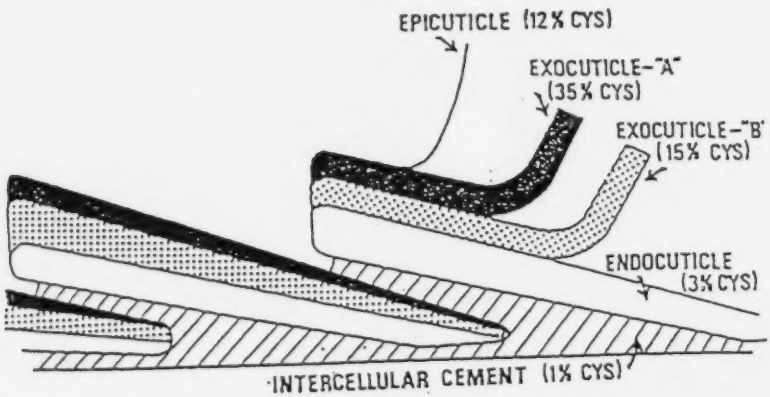


Figure 2: Schematic of wool fibre cuticle

Note. From "The Cell Membrane Complex and Its Influence on the Properties of the Wool Fibre" by J. D. Leeder, 1986, Wool Science Review, 63, p. 15. Copyright 1986 by the International Wool Secretariat. Reprinted by permission.

The Cortex

The cortex is made up of the cortical cells and the cell membrane complex.

Cortical cells. The cortical cells are long, narrow, spindle shaped cells, that make up 90% of the wool fibre mass (Alexander et al., 1963, p. 3; Ito, Sakabe, Miyamoto, & Inagaki, 1984; Maclaren & Milligan, 1981, p. 3). They are approximately 85-120 μm in length and 4.6-6 μm in width (Marshall et al., 1991). The cortical cells are aligned longitudinally in the fibres.

The α-keratin protein molecule is an α-helix, the axis of which is nearly parallel to the fibre axis. Two of the individual helices are wound together into protofibrils, 2 nm in diameter (Watt, 1980). Nine of these highly crystalline protofibrils, in turn, are wound together into crystalline microfibrils, also referred to as intermediate filaments (IFs), which have both helical and non-helical regions, and are approximately 7.5 nm in diameter (Marshall et al., 1991). The IFs are about 10 nm (100Å) apart (Chapman, 1969) and are surrounded by the matrix, an amorphous region of less order than the microfibrillar regions containing most of the cysteine residues (Marshall et al.; Watt). The intermediate filaments pack together into macrofibrils, which in turn make up the individual cortical cells. It is not known if the polypeptides of the IFs are crosslinked to each other. Marshall et al. [referring to Fraser et al. (1988) who investigated the locations of disulphide bonds within the IFs] concluded that crosslinking between the IFs seems unlikely.

The matrix can be regarded as a crosslinked polymer held together by a network of H-bonds and salt linkages (Chapman, 1969). This amorphous area tends to be highly absorbent (Marshall et al., 1991). The relatively disordered structure of the matrix allows it to be penetrated and weakened by small water molecules more easily than the microfibrils (IFs) (Chapman).

There are two types of cortical cells, the orthocortical and the paracortical, which differ slightly in chemical make-up and reactivity (Cook, 1968, p. 99). The ortho- and para-cortices are arranged bilaterally. Marshall et al. (1991) suggest that the paracortex contains more matrix material, and higher concentrations of high-sulphur proteins than the orthocortex. The macrofibrils of the orthocortex are discrete and twisted along the axis whereas the paracortex macrofibrils appear to be fused and poorly defined, especially around the cell periphery (Marshall et al.). The orthocortical cells have a larger cross-sectional area than the paracortical cells and are the predominant cell type making up greater than 50% of the fibre cross-section and volume (Marshall et al.). The differences in structure and reactivity of the orthocortex and paracortex result in the characteristic crimp in wool fibres.

Cell membrane complex. The cuticle and cortical cells are bound by membranes which together with the intercellular material are the cell membrane complex (CMC) (Marshall et al., 1991). The CMC makes up 6% of the fibre and is the only continuous phase in the wool fibre (Leeder, 1986). The CMC has three components described by Leeder: a soft, easily swollen intercellular cement of lightly crosslinked protein; a lipid layer; and a chemically resistant protein membrane surrounding each cortical and cuticle cell (this includes the epicuticle). Maclaren and Milligan (1981, p. 3) describe the roles of the CMC as separating the cuticle cells from the cortical cells, surrounding the cortical cells and cementing the cells together.

A small portion of the fibre mass (≈3%) is the intercellular cement, a nonkeratinous protein material with high levels of glycine, tyrosine and phenylalanine (Leeder, 1986). The intercellular cement is considered to be "sandwiched" between the resistant cell membranes of neighbouring cortical cells (Bradbury, Leeder, & Watt, 1971). Measurements from transmission electron micrographs determined the thickness of the intercellular cement to be 15 nm (Leeder).

The intercellular cement of the CMC has a low cysteine content and therefore few disulphide bonds (Leeder, 1986). Disulphide bonds usually serve to restrict fibre swelling. The low disulphide bond content in the intercellular cement suggests that these regions are susceptible to swelling and may be easily modified (Leeder). It is expected that moisture absorption in the wool fibre first occurs in the intercellular cement.

The lipid content of the wool fibre is in the range of 1% (Rivett, 1991) to 1.5% (Leeder, 1986). Three major lipid classes are found in a typical wool fibre: sterols (40%), consisting predominantly of cholesterol and demosterol; polar lipids (30%), consisting of cholesterol sulphate, ceramides and glycosphingolipids as well as small amounts of sphingolipids; and fatty acids (30%), predominantly stearic, palmitic, 18-methyleicosanoic and oleic acids (Rivett). The presence of a lipid bilayer in the CMC is uncertain. Most evidence indicates that a lipid bilayer is unlikely (Leeder; Rivett). However, if a lipid bilayer is in fact present, and able to split along the junction of nonpolar ends, it is expected that this would have an effect on the mechanical and chemical stability of the fibre (Leeder).

The wool fibre has a resistant membrane content of ≈1.5% (Leeder, 1986). The resistant membranes surround the individual cortical cells. They contain approximately the same proportion of cystine crosslinks as whole wool (≈12%), and the reason for their extreme chemical inertness is not known (Leeder). The high level of lysine in the membranes has led to the suggestion that isopeptide crosslinks (eg. ε-[γ-glutamyl]-lysine crosslinks) between lysine and glutamic acid side chains may contribute to this chemical stability (Leeder). Because these membranes are chemically inert and surround the cell content, their physical and chemical stability govern the integrity of the cells and the fibre as a whole (Matoltsy cited in Leeder, p. 12).

In summary, the cell membrane complex is a weak region with low mechanical and chemical stability (Leeder, 1986). Leeder (p. 17) states that "because it is a weak link, it assumes an important role in both the physical and chemical behavior of the fibre". Individual cortical cells may be separated by damaging the cell membrane complex (Maclaren & Milligan, 1981, p. 3).

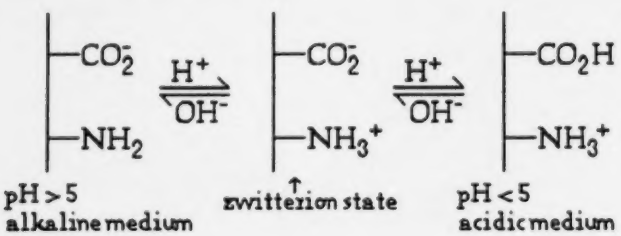
Properties of Wool

Chemical Properties

Wool is degraded primarily by high pH (alkaline) conditions. Mildly acidic conditions are generally not degrading to wool (Alexander et al., 1963, p. 291). Wool is resistant to most mineral acids except for hot sulphuric and nitric acids (Cook, 1968, p. 107). Chemical degradation is due to breaking of the inter- and intra- molecular bonds: the salt-links, hydrogen bonds, disulphide bonds, and peptide links, generally in this order.

The amino acids in wool have both basic and acidic side chains; therefore, the wool molecules are considered to be amphoteric, they are capable of combining with both acids and bases (Alexander et al., 1963, p. 180; Maclaren & Milligan, 1981, p. 9). Overall, wool is basic in character due to the predominance of the side chains of the arginine, lysine, and histidine amino acids (Maclaren & Milligan, p. 9). At the isoelectric point, the molecule is in the

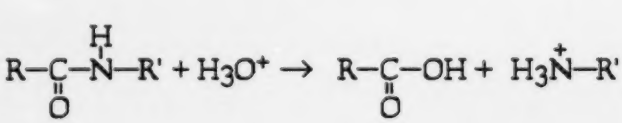
zwitterion state where all of the groups are ionized and the sum of positive and negative charges on the amino acids is zero (Mathews & van Holde, 1990, p. 33; Dusenbury, 1963, p. 237). The isoelectric point of wool is approximately pH 5. Conditions above pH 5 are considered alkaline to wool. The uptake of acid results in the progressive conversion of carboxylate anions (COO^-) to carboxylic acid (COOH), while the uptake of alkali converts the charged amino (NH_3^+) groups to the unionized state (Maclaren & Milligan, p. 110) (Equation 2). High salt concentrations will reduce the isoelectric range (Alexander et al., p. 182).



[2]

Hydrolysis

The peptide links of the protein chain are very stable although they can be hydrolyzed by acids, alkalis and enzymes as illustrated in Equation 3 (Alexander et al., 1963, p. 288). Cleavage of the peptide bonds increases the solubility of wool (Marshall et al., 1991). If the molecular chain of the protein is broken at the peptide bonds, the remaining polypeptides may be solubilized more readily. The extent of hydrolysis depends on the severity of the conditions used (Maclaren & Milligan, 1981, p. 110). Enzymatic hydrolysis by proteolytic enzymes generally cleaves only main chain peptide bonds (Maclaren & Milligan, p. 269).



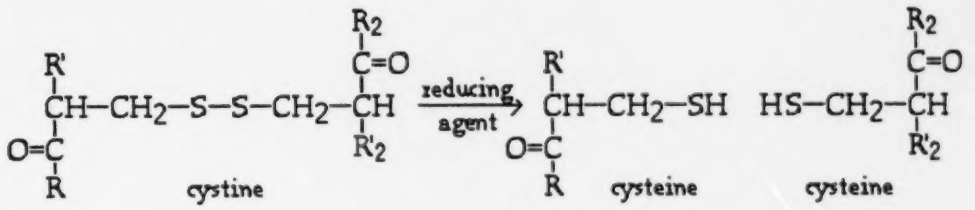
[3]

Disulphide Bond Reactivity

The highly crosslinked hard keratins can only be appreciably solubilized if covalent bonds are broken (Marshall et al., 1991). The disulphide crosslinks lead to the characteristic

insolubility and chemical inertness of the fibre. These crosslinks render keratin insoluble in water (Watt, 1980). The disulphide bonds can be intra- or inter- molecular.

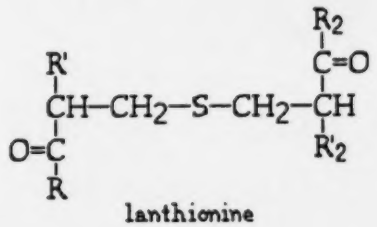
Alkaline conditions can lead to breakage of the disulphide bond (Alexander et al., 1963, p. 210). Treatment of wool with reducing agents, such as thiols and phosphines, converts the disulphide groups to thiol groups, each cystine residue giving two cysteine residues (Equation 4) (Maclaren & Milligan, 1981, p. 19):



[4]

Reduced disulphide bonds may be readily reoxidized unless they are blocked.

Alkaline treatment of wool also causes formation of lanthionine crosslinks containing one sulphur atom from the original cystine disulphide bonds (Equation 5) (Dusenbury, 1963). The mechanism of the reaction by which lanthionine is formed as a result of the alkaline decomposition of disulphides is uncertain (Dusenbury; Maclaren & Milligan, 1981, p. 101). Lanthionine crosslinks are stable to reducing agents (Maclaren & Milligan).



[5]

Relatively small extents of reduction are required to produce noticeable changes in fibre properties (Maclaren & Milligan, 1981). Because the matrix and microfibrils are structurally interdependent, when disulphide crosslinks in the matrix region are reduced, this change will decrease the stability of the helical protein chains within the microfibrils (Menefee, 1977).

Reduction of the disulphide bonds takes place in the same proportion in both high and low sulphur components of the keratin structure (Chapman, 1969).

Properties of the Cell Membrane Complex

The CMC has a major influence on fibre properties. Its components can affect mechanical properties, like abrasion resistance; chemical properties, such as susceptibility to attack by acids; and the diffusion of dyes and other molecules into and within the fibre. The CMC acts as the adhesive between the individual cuticle and cortical cells. Leeder (1986) compares the relationship of cortical cells with the CMC to that of bricks and mortar. Damage to the CMC causes the fibre to fall apart: "When wool fibres break down under repeated cyclic stress ... they do so by preferential splitting along weak boundaries within the fibre" (Leeder, p. 22). The weakness of the intercellular cement and damage to this component of the fibre affects the properties of the fibre as a whole. It is suggested that severe damage to the wool fibre occurs first in the intercellular cement.

The protein layer between the cuticle cells, because of its low cystine content, should be capable of swelling to a very high degree compared with the whole fibre or any of the cuticle components. Disproportionate swelling of the intercellular cement provides support for suggestions that the CMC could form channels for diffusion of molecules into the fibre (Leeder, 1986).

Degradation of Wool by Microorganisms

Wool generally exhibits high resistance to microorganisms (Lewis, 1981, p. 103). The high sulphur content of the fibre may be the reason for this as the disulphide bonds are relatively resistant to proteolytic enzymes (Lewis, p. 82). Natural fibres, however, are eventually decomposed by microbes (McCarthy & Greaves, 1988, p. 28). Impurities such as soaps, natural oils, or perspiration on the fibres initially attract and support the growth of moulds and bacteria (Lewis; McCarthy & Greaves; Nopitsch, 1953). Eventually, the enzymes

produced by the microorganisms (eg. trypsin) will begin to digest the wool fibre. The enzymes digest only the amorphous protein in the scales and the cell membrane complex between the cells (Leeder; Nopitsch). The weakening and dissolving of the CMC results in the cortical cells becoming separated (Lewis, p. 82; Nopitsch). This separation is also known as fibrillation. The ortho- and paracortical cells cannot be digested by proteolytic enzymes unless the disulphide bonds have been ruptured by oxidation and reduction processes (Lewis, p. 82).

The proteolytic enzymes produced by microorganisms are affected by temperature, moisture content, pH and the oxidation-reduction potential of the system (Lewis, 1981, p. 84). The rate of microorganism growth is enhanced by warmth (25 to 40 °C) and moisture is normally the principal parameter determining microbial growth (McCarthy & Greaves, 1988, p. 41). In order for bacteria to attack wool, the moisture content must be a minimum of 40% (Lewis, p. 99; Nopitsch, 1953), thus, the wool must be wet. Mildew requires lower moisture content in wool, only about 25%, and therefore a high relative humidity, above 85% (Lewis, p. 99). Most microorganisms are dormant at temperatures below freezing; however, many species' spores will survive freezing and pose a potential danger upon thawing (Davies & Obafemi, 1985). A sign that there may be bacterial damage is tendering or premature wear of the fabric (Nopitsch). Microscopically, fibrillated fibres and frayed, brush-like fibre ends are evidence of damage by bacteria.

Physical Properties of Wool

The physical properties of wool fibres, such as strength, extension and recovery, arise from the properties of the fibres' component parts (Marshall et al.,1991). The properties of the filaments and matrix, such as filament length, filament orientation and packing, proportion of matrix, and adhesion of the matrix to the filaments all contribute to the physical properties of the fibre as a whole. The molecular structure of these components will, for a large part, determine the properties of each. The length of the molecular chains, the arrangement of

molecular chains, and the intermolecular bonds within a fibre and its component parts all play a role in determining the fibre's properties.

Protein fibres with folded molecules, such as wool, are characterized by low strength but great extensibility. The folds of the molecules can open up as a load is applied to give the fibre high extensibility (Morton & Hearle, 1975, p. 55). As the wool fibre is extended, there is a stretching out of the α-helical structure to the β-pleat structure of keratin. The helical turns of the molecular chain, however, contribute to the weakness of the fibre. A tensile load is not distributed evenly along the "backbone" of the chain. As well, the low disulphide content of the intercellular cement makes it a weak region in the fibre and contributes to the weakness of the fibre as a whole. The numerous disulphide crosslinks, hydrogen bonds, and salt links of keratin protein contribute to the excellent elastic recovery and resiliency of wool (Joseph, 1981, p. 54; Mathews & van Holde, 1990, p. 183).

As a tensile force is applied to a fibre several changes occur. Initially, the crimp in the fibre is removed and the fibre is aligned and straightened in the direction of the applied force. At this point the fibre is fairly stiff and a rapid increase in force occurs with little increase in fibre extension (Chapman, 1969). The molecular chains in the amorphous regions and the intermolecular bonds in the fibre are stretched and better aligned but not broken; this is a region of complete elastic recovery (Merkel, 1991, p. 167). Beyond 2% extension and up to approximately 30% extension, the fibre begins to yield, actual breakage of intermolecular bonds in the fibre occurs and there is extensive movement of molecules within the amorphous regions (Merkel). Rapid extension occurs with little change in stress (Chapman). With this rearrangement of molecules new attractive forces between molecular chains form and the fibre is in a better position to withstand further stresses. The rate of extension decreases as stress continues to increase. Eventually, the fibre becomes stiffer, crosslinks are broken, the main molecular chains break and the fibre fails.

The tensile properties commonly reported are tensile strength, extension at break, and work of rupture or energy at break. Compared to other fibres, such as silk, nylon, and cotton,

wool is weak. It is one of the weakest textile fibres (Joseph, 1981, p. 54) with a comparatively wide range in fibre strength (Marshall, Orwin, & Gillespie, 1991). The tensile strength of a wool fibre is 0.11 to 0.14 Newtons per tex when dry, and 0.08 to 0.10 Newtons per tex when wet (Morton & Hearle, 1975, pp. 282 & 293). Breakage of the fibre usually occurs around 25-35% extension (Cook, 1968). Table 2 summarizes typical values for some physical properties of wool fibres.

Energy at break, or work of rupture, is a measure of overall toughness of a fibre, taking both breaking strength and extension at break into account. It is a measure of the amount of energy required to stretch a fibre or yarn to the breaking point. It is determined by calculating the area under the stress-strain curve. Changes in the tensile strength or the elongation at break (or both) can affect the energy at break (Morton & Hearle, 1975).

Table 2
Physical Properties of Wool Fibres

Property	Typical Value
Density	1.30 - 1.32 g/cm^3 [a]
Refractive Index	$n\parallel = 1.553$ [b] $n\perp = 1.542$ [b]
Birefringence	$\Delta n = 0.010$ [b]
Tenacity	0.11 - 0.14 N/tex [b]
Wet Strength	0.08 - 0.10 N/tex [b] (69% of dry strength)
Breaking Extension	25-35% dry [c], 40-60% wet [b]
Work of Rupture	30.9 mN/tex [b]
Initial Modulus	2.3 N/tex [b]
Elastic Recovery (2% extension)	99% [a,c]
Moisture Regain (at 65% RH, 20°C)	16-18% [b,c]
Swelling in Water	25-26% increase in total volume of fibre [b] 15-17% increase in fibre diameter [b]

[a] Joseph (1981, p. 55), [b] Morton and Hearle (1975), [c] Cook (1968)

The moisture content of wool has a major influence on its physical properties (Watt, 1980). The sorption of water by wool results in a general weakening of the fibre (Windle, 1956). This is attributed to the swelling action of the sorbed water which is assumed to break the bonds which contribute to the strength of the fibre. Water acts as a plasticizer allowing molecules in the fibre to move more easily. An increase in water content leads to the breakdown and reformation of bonds in the microfibrils reducing the resistance to longitudinal stresses (Watt). It is also assumed that increased water content further weakens the intercellular cement. The lack of strong disulphide bonds in the intercellular cement permits ease of swelling and breakage of hydrogen bonds and salt-links in this region.

Wool has a high moisture regain value. It is able to absorb up to 33% of its weight in moisture without feeling wet (Alexander et al., 1963, p. 87; Watt, 1980). The water content of keratin is influenced by humidity and temperature, however treatment history, wool type, and the method by which equilibrium relative humidity is approached (eg. adsorption vs. desorption) can also influence water content values (Watt). The wool-water relationship is discussed in more detail later in this chapter.

Methods Used to Evaluate Selected Physical and Chemical Properties of Wool

Methods used for the evaluation of wool properties are few. A combination of methods is often advised for evaluating changes or damage in wool textiles. These methods include evaluation of physical, chemical, and appearance properties.

Tensile Testing

Tensile testing is perhaps the most widely used physical method for determining the degree of damage in textile materials. Changes in the microstructure of a fibre will often show up in changes in the physical properties of the fibre (Maclaren & Milligan, 1981). However, tensile testing is not a highly sensitive method (Maclaren & Milligan); changes in fibre structure will have to be severe before there are significant changes in tensile properties.

Ideally, tensile testing would be performed at the fibre level for optimum determination of changes in the fibre microstructure. This is often not possible; therefore, yarn or fabric tests may be used. The stress-strain curves of yarns and fabrics show some of the same characteristics as the curves for fibres (Merkel, 1991). Some differences in curves (for the same fibre type) will be due to structural arrangement, such as the amount of twist in a yarn or the density of fabric weave. The fibre properties will give a limit to what is possible in a yarn or fabric. In staple fibre yarns, the yarn strength can never be more than the strength of the fibres in the yarn (Merkel, p. 110-111; Morton & Hearle, 1975, p. 265). In twisted staple fibre yarns, failure is only due partly to fibre failure, after some of the fibres break, the yarn structure becomes loosened and the remaining unbroken fibres slip apart. However, Cook and Fleischfresser (1990) state that "although the values of strength and extension at break obtained with yarn will not be identical to those with single fibres, the trends obtained with a given yarn nevertheless reflect single fibre properties and provide useful insight into the failure behavior of wool".

The tensile properties determined are usually breaking strength and elongation which are tested concurrently. Sometimes energy at break or work of rupture is calculated and reported. Several methods for testing yarn tensile strength are available. In Canada, CAN/CGSB-4.2 No. 9.4, "Breaking Strength of Yarns - Single Strand Method" or ASTM method D 2256-88 "Tensile Properties of Yarns by the Single-Strand method" are frequently used.

Chemical Testing

The methods for evaluating the chemical properties and changes in the molecular structure of wool fibres include staining techniques, amino acid analysis, and solubility testing.

There are a variety of staining techniques used for protein fibres (Merkel, 1984). These include: the methylene blue test, which tests for oxidation of wool; the kiton red test, to test for damage to the epicuticle of the fibre; and the lead acetate test, which is used to determine a

change in the oxidation state of sulphur in wool (Merkel). Each of these tests requires comparisons between undamaged control and treated or damaged wool.

Amino acid analysis is used on protein fibres to determine changes in the amino acid content or composition of the fibres. Proteins are subject to hydrolysis and the reduction in molecular chain length due to degradation may be detected by increased quantities of amino (NH_2) groups. The ninhydrin method is used to determine the presence of amino groups (Knott, Grandmaire, & Thelen, 1981). The more amino groups that are present, the more the chains have been broken; thus, the relative degree of fibre damage may be evaluated by comparison to the control standard. The method has been used on silk in textile conservation research (Kuruppillai, Hersh, & Tucker, 1986; Miller, 1986); however, it may also be used on wool (Knott et al.; Wang & Pailthorpe, 1987).

Solubility tests are commonly used to determine changes in the chemical structure of wool and are based on a change in weight after the fibre is treated with specific solubilizing agents. The nature of the changes may not necessarily be determined by solubility testing; however they may give an approximation of the degree of fibre damage at the molecular level. Alkali solubility tests for determining the extent of oxidation were first introduced by Harris and Smith (1936). Lees and Elsworth (1952) concluded that both breakdown of disulphide linkages and hydrolysis of the peptide chains result in an increase in alkali solubility. The urea-bisulphite solubility test is a common solubility method which is sensitive for measuring changes that occur when wool is treated with certain chemical reagents. A decrease in urea-bisulphite solubility may be attributed to the transformation of intra-chain disulphide linkages to inter-chain linkages as a result of chemical treatment (Lees, Peryman, & Elsworth, 1960).

The tributylphosphine-alcoholic sodium iodide (TASI) solubility test is a relatively new solubility method that has been used to some extent by wool researchers (Jones & White, 1971; Kearns & Maclaren, 1979; Kilpatrick & Maclaren, 1970). It is based on the swelling and extraction of wool in an aqueous ethanolic solution of sodium iodide. The addition of

tributylphosphine causes the reduction of cystine crosslinks. After the cystine crosslinks have been broken, the extent of hydrolysis of the main chains in the protein is reflected in the mass of fibrous protein remaining after filtration (Brown, 1972; Kilpatrick & Maclaren).

The TASI solubility method is sensitive to modification of the wool and has been used to study changes caused by scouring, hot water, mild alkali and formaldehyde treatments. The reagent is neutral; lanthionine crosslinks are retained and no further degradation occurs. It is more sensitive than other frequently used solubility methods such as the urea-bisulphite or alkali solubility tests and duplicate measurements show high reproducibility (Kilpatrick & Maclaren, 1970). Typical solubility results for new wool range from 59% to 72% soluble matter extracted (Jones & White, 1971; Kearns & Maclaren, 1979; Kilpatrick & Maclaren). Brown (1972) noted that "it would be interesting to extend this test to a wider range of treatment conditions".

Observational Methods

Perhaps the most widely used method for the qualitative evaluation of fibres is the use of the standard laboratory, light microscope. Basic microscopic observation may provide general information regarding the fibre's structure and changes that occur as a result of various treatments. More sensitive observations are possible with a scanning electron microscope (SEM) which allows for very high magnification, larger depth of focus than a light microscope, and great clarity of surface detail (Morton & Hearle, 1975, p. 21). SEM observation provides a means for qualitative evaluation of changes in a fibre's surface characteristics. A reference collection of SEM photomicrographs of textile fibres exposed to various known damaging forces was compiled by Hearle, Lomas, Cooke, and Duerdon (1989). Researchers may be able to hypothesize the cause of damage to textile fibres by using the photomicrographs of fibres with known sources of damage as standards for comparison.

The Wool-Water System

The dominant role that water plays in influencing the physical properties of wool fibres and its role in the preservation of biological materials in freezing warrant a closer examination of the interaction of water with the wool fibre. The wool-water system is a complex system that is not yet fully understood (Watt, 1980). Wool is an absorbent material and the sorption of water vapor depends upon many factors. In order to explain the wool-water system, the properties of water will be examined. The relationship between moisture sorption and equilibrium relative humidity will be discussed. The distribution of water within the wool fibre will be examined. Finally, swelling of the wool fibre as the result of water sorption will be addressed.

Properties of Water

Water (H_2O) is composed of small polar molecules having a molecular weight of 18.02 g/mole, and diameter of 0.25 nm (2.5 Å). Water molecules have high hydrogen bonding capacity. Hydrogen bonds are the result of an unusually strong coulombic attraction between a partial positive charge on the hydrogen atom and a partial negative charge on the atom of the more electronegative element with which the bond is forming (eg. oxygen) (Boikess & Edelson, 1985, p. 425). A hydrogen bond is substantially weaker than a covalent or ionic bond, but is substantially stronger than other, weak interactions such as dipole-dipole interactions. In water, the hydrogen atom of one water molecule attracts the oxygen atom of another and a bond is formed. When hydrogen bonding occurs it plays a dominant role in determining intermolecular properties, such as the high boiling point of water (Barrow, 1973, p. 518).

The water molecule acts as both a "donor and an acceptor" of hydrogen bonds (Boikess & Edelson, 1985, p. 426). Each water molecule has two hydrogen atoms and two non-bonding valence electron pairs on the oxygen atom and can therefore form four hydrogen bonds. Each oxygen atom of a water molecule will be surrounded by four hydrogen atoms (Figure 3). The

hydrogen bond may also form between the hydrogen of water and the nitrogen of an amino group or the oxygen of a carboxyl group, or between the amino and carboxyl groups (Figure 4).

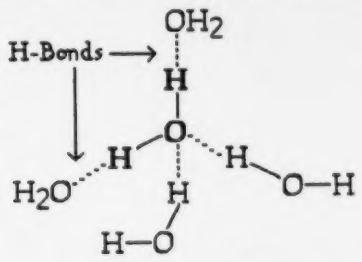


Figure 3. Example of 4 possible H-bonds with one water molecule (Boikess & Edelson, 1985).

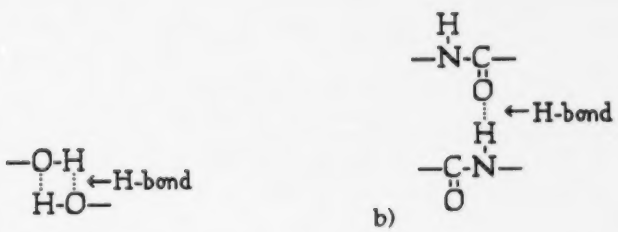


Figure 4: Examples of hydrogen bonding: a) between hydroxyl groups and b) between amino and carbonyl groups.

Water as a Plasticizer

A plasticizer can be described as a material which, when incorporated into a polymer, increases that polymer's workability, flexibility, or extensibility (Slade & Levine, 1991). Water sorbed by polymers often plays a plasticizing role. A fluid environment allows molecular mobility and liquid water is well suited to this purpose (Mathews & van Holde, 1990). The low molecular weight of water allows it to easily be sorbed into amorphous and partially crystalline polymers. Increased water content leads to increased mobility of molecular chains in the amorphous regions of a polymer. This is due to the increased molecular space and decreased local viscosity imparted by the highly mobile water molecules (Slade & Levine).

Equilibrium Moisture Content and Sorption Isotherms

An item will gain moisture from the atmosphere until it reaches an equilibrium value, the equilibrium moisture content (Labuza, 1984). (Moisture content is also known as "moisture regain" in textile terminology and the terms are often used synonymously, even though the standard textile definition differs.) For a keratin-water vapor system in equilibrium, there is a balance between the number of water molecules entering and leaving the keratin and that number is proportional to the relative humidity (Watt, 1980).

The relationship between the equilibrium moisture content of wool and the relative humidity of the environment at a constant temperature is expressed in the water vapor sorption isotherm (Watt, 1980). Moisture content (or moisture regain), as measured by the change in fibre weight from a dry condition to equilibrium at a given relative humidity, is plotted against a range of relative humidities. The result is a sigmoidal isotherm curve similar to the one shown in Figure 5.

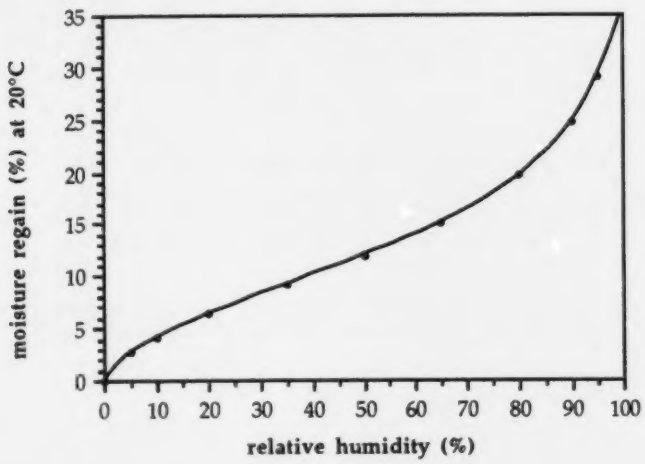


Figure 5: Moisture sorption isotherm for wool at 20°C from the data of Watt & D'Arcy (1979).

There is good agreement between published sorption isotherms for wool at temperatures close to room temperature; however, above 50°C, the factors affecting sorption have greater influence and considerable variability in results exists (Watt, 1980). This is partly due to

degradation of wool by water vapor at high temperatures (eg. above 55°C), as found by Speakman and Cooper (1936). As well, increased swelling at higher temperatures affects the amount of water sorbed by wool (Speakman & Cooper). Temperature affects the mobility of water molecules and the dynamic equilibrium between the vapor and absorbed phases of the water (Kapsalis, 1987). At high temperatures the water molecules are more mobile and able to penetrate the molecular structure more easily and quickly than at low temperatures.

Reliable moisture regain values for wool at 0% and 100% relative humidity are difficult to obtain (Watt, 1980). Although numerous different drying methods have been employed, varying amounts of residual water remain in the keratin at 0% relative humidity. The residual water is strongly bound to high energy hydrophilic sites of the wool molecules. It is believed that water bound at these high energy sites is never completely removed. The high temperatures required to remove this residual water lead to the decomposition of the fibre and a subsequent loss of weight due to protein degradation (Watt).

It is also difficult to obtain values for the water content of wool at 100% relative humidity. Lynch and Webster (1979) found that it was difficult to maintain stable vapor pressure near saturation; and moisture regain is extremely sensitive to the slightest variation in humidity near saturation (Watt, 1980). Watt also states that the water content at 100% relative humidity increases with time. At high relative humidities, the water molecules have great mobility and may move in and out of the fibre with little resistance, making it difficult to obtain constant conditioned weights. As well, at 100% relative humidity, condensation will occur. Water may condense in the inter-fibre spaces of fibre bundles. This water is not adsorbed within the fibres and, if included in the conditioned mass, misleading regain values at 100% relative humidity can result (Watt).

Sorption Processes

Water molecules enter the wool fibre via diffusion. This diffusion is driven by the concentration gradient between the fibre and the external environment established when the

water molecules are initially sorbed at the wool surface (Watt, 1980). The water molecules diffuse from the surface of the fibre to its interior via fine capillaries, such as the pores in the cell membrane complex; adsorption along the interfaces between the morphological components; and the penetration of water molecules in the amorphous regions (D'Arcy & Watt, 1981).

Because moisture sorption is a diffusion driven process, changes in relative humidity change the concentration gradient, thus affecting the sorption and binding of water molecules in the wool fibre. At low relative humidity, proteins absorb water molecules by binding them to the strongly hydrophilic sites. As the humidity increases, condensation or multimolecular absorption occurs (Leeder & Watt, 1965). At high relative humidities, water molecules bind to the other water molecules already bound and form a hydrogen bonded network (Watt, 1980). Solution or condensation absorption becomes a measurable component of the water content at 80% relative humidity when incoming molecules condense on water already present in the wool (Leeder & Watt).

The degree of change in relative humidity that a substrate (eg. wool) is exposed to in a sorption/desorption study will determine if sorption occurs via one *integral* step or via *interval* steps. *Integral* sorption occurs when wool is subjected to a particular relative humidity in one step, generally a change greater than 15% RH. *Interval* sorption, or two-stage uptake, occurs with small changes in relative humidity, eg. increments less than 15% RH (Watt & D'Arcy, 1979).

Wool exposed to small relative humidity increments (*interval* sorption) may attain a higher water content value than that achieved by a single step to that humidity (Watt & D'Arcy, 1979). When a small incremental step is applied, initial uptake of water vapor by diffusion introduces stresses to the H-bonded substrate which relax by bond breakage and reformation processes. In the second stage, in order to maintain thermodynamic equilibrium between the sorbed water and the external environment, further water is taken up allowing additional swelling of the polymer and configurational changes within the fibre (Watt, 1980). Although the first stage is rapid, the second stage may occur over several days (Watt &

D'Arcy; Watt). For *integral* sorption from the dry state to a particular relative humidity, the stresses introduced by the rapidly sorbed water are great and the molecular network is disrupted such that stress-relaxation occurs so rapidly that equilibrium is often obtained within 30 minutes (Watt & D'Arcy; Watt).

Hysteresis in Moisture Sorption-Desorption

In moisture sorption isotherms, desorption isotherms give higher water content values than adsorption or absorption isotherms at the same relative humidity and temperature (Figure 6). This phenomenon is known as "moisture sorption hysteresis" and is characteristic of polymers which swell with the adsorption of water. For wool- or keratin-water vapor isotherms, hysteresis is usually displayed over the entire humidity range and is dependent upon the previous sorption history of the wool (Watt, 1980). Because of poor agreement among desorption isotherms, their use is inappropriate for the determination of equilibrium water content in the analysis of water vapor sorption isotherms (D'Arcy & Watt, 1981; Watt). In wool, hysteresis can be eliminated by desorbing from saturation directly to a dry state then determining water content at the desired relative humidity (Kapsalis, 1987; Watt & D'Arcy, 1979), preferably using an integral sorption process (Watt & D'Arcy).

Hysteresis is a phenomenon that is not fully understood (D'Arcy & Watt, 1981; Kapsalis, 1987; Slade & Levine, 1991; Watt, 1980). Several theories attempting to explain sorption hysteresis have been proposed (D'Arcy & Watt; Kapsalis; Slade & Levine; Watt). The most recent theories attribute hysteresis to molecular rearrangement and relaxation processes which occur due to the plasticizing effects of water (D'Arcy & Watt; Slade & Levine; Watt). In the saturated swollen state, water molecules are mobile and more binding sites are available to additional water molecules than are available in the unswollen fibre (Slade & Levine; Watt). These sites continue to bind the water molecules as the relative humidity is lowered (Watt). The magnitude of the desorption step and the rate at which water can be removed from the substrate (influenced by packing density of the fibres or yarn structure) both

contribute to the amount of water retained (D'Arcy & Watt). The lower water content values of adsorption isotherms are attributed to much slower relaxation of the molecules in the wool on adsorption of water vapor (than on desorption) (Slade & Levine; Watt). To summarize: Hysteresis results from a swelling induced conformational change which is dependent on moisture, time, and temperature; the change is brought about by the increasing free volume and increased mobility of polymer molecules which results from the plasticizing action of sorbed water (Slade & Levine, p. 266).

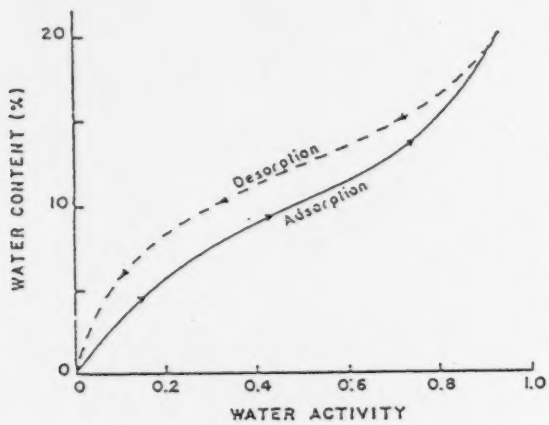


Figure 6: Sorption isotherm illustrating hysteresis

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Water Activity

Water is considered to be a major control component in mass transfer, chemical reactions and the activity of microorganisms (LeMaguer, 1987). "Water activity" refers to the water in a system which is available for reactions, whereas water content is the total amount of water in that system, all of which may not participate in reactions (Troller, 1983). Generally, the higher the water activity, the faster the reaction rate because of the greater solubility and

increased mobility of reactants (Labuza, 1984). However, there is no formal cause and effect relationship between a reaction rate and water activity (Slade & Levine, 1991, p. 122).

The water activity of a material in a controlled atmosphere is generally considered to be the same as the water activity of the air in that atmosphere. Water activity can be determined from the equilibrium relative humidity (Labuza, 1984) using the relationship:

$$\text{water activity} = \%RH/100 \qquad [6]$$

A typical sorption isotherm of moisture content vs. water activity (Figure 6) resembles the isotherm of moisture regain vs. relative humidity (Figure 5). The difference between the two plots is that equilibrium relative humidity is 100x greater than water activity. Techniques for measuring water activity require that the vapor pressure or some parameter which can be related to vapor pressure, such as relative humidity, must be determined (Troller, 1983). Slade and Levine (1991, p. 121) question this relationship by stating that "relative humidity in the headspace over a food product is actually an *apparent* relative vapor pressure which cannot then be related to water activity which is "a thermodynamic quality". Current theorists identify water activity as "a thermodynamic concept rigorously applicable only to dilute aqueous solutions at equilibrium" (Slade & Levine, p. 124). According to Slade and Levine the use of the term "water activity" is questionable and its application to intermediate and low moisture food products is considered inappropriate. Textile researchers evaluate moisture content (or moisture regain) strictly in terms of relative vapor pressure or relative humidity. However, the water activity value as a measure of relative vapor pressure is useful in calculating an estimate of bound water using the BET equation which will be described later.

Moisture Sorption in Wool

Both the physical and chemical properties of wool contribute to its moisture sorption. Wool has both water-accessible (amorphous) regions and water-inaccessible (crystalline) regions (Watt, 1980). Small water molecules may readily gain access to the internal structure of keratin protein (Watt) and will be sorbed in the amorphous intercellular cement and the

matrix. Water molecules will sorb to the surface of a crystalline region (eg. the protofibrils) but generally will not penetrate that region (Feughelman, 1989).

Water molecules tend to align along the protein molecules parallel to the fibre axis (Watt, 1980). Adsorbed water causes a separation of neighbouring polypeptide side chains allowing a second layer of water to be absorbed. The water is not uniformly distributed within the cortical cells but preferentially associates with regions external to helical material (Haly & Snaith, 1968), primarily in the matrix and intercellular cement. Pore diameters in the amorphous regions of the cortical cell matrix have been reported as 4 nm (40 Å) (Alexander et al., 1963, p. 388). These pores provide spaces for the water molecules so that they may bond to the hydrophilic groups of the wool protein. References to the size of pore diameters in the intercellular cement have not been found. Water sorbed above 80% relative humidity is predominantly associated with the matrix (Watt).

Crosslinks which provide resistance to swelling, and the subsequent increase in the size of spaces in the fibres, prevent water uptake. Salt bridges between the carboxylate anions (COO-) and charged amino groups (NH_3^+) decrease the water uptake (Watt, 1980) and sulphur crosslinks also restrict the size of the spaces available to water molecules. This suggests that the matrix, with its high sulphur content, is less easily swollen and has smaller spaces for water molecules than the low sulphur intercellular cement. The wool fibre is highly amorphous and because the intercellular cement makes up only 3% of the fibre, it can be seen that sorbed water would be found primarily in the matrix.

Adsorbed water in keratin is associated with the hydrophilic groups: the polar side chains and the peptide groups of polypeptide chains. The free amino, carboxyl, and hydroxyl groups of the amino acid side chains are the main polar groups in proteins (Leeder & Watt, 1965) and at relative humidities up to 65%, water associates with these groups which are the most readily available. The initial water sorbed by dry wool is associated with these strongly hydrophilic groups which contribute to water sorption to the greatest extent (Leeder & Watt; Watt, 1980). All the amino groups of the side chains are equally accessible to water vapor

despite the complex morphological structure of wool (Leeder & Watt). Ionized amino and carboxyl groups of the polar side chains have similar strength of adsorption at low relative humidities (below 50% RH) and are strong hydrogen bonding sites for water molecules (Watt).

The contribution of the polypeptide chain becomes progressively more important at higher humidities (Kapsalis, 1987). Once the initially sorbed water molecules have bound to the hydrophilic groups of the side chains, the next water molecules bind to the carbonyl and amino groups of the peptide chain. Sakabe, Ito, Miyamoto, and Inagaki (1987) concluded that at high water contents the peptide groups of the main chain play the most important role as water binding sites. At 80% relative humidity, the peptide bonds account for almost half of the binding sites of the sorbed water, where the the water tends to be associated with the carbonyl groups (Watt, 1980).

Binding of Water in Wool

Water molecules have a high hydrogen bonding capacity and there is strong energy of association between absorbed water molecules and the hydrophilic sites on keratin (Watt, 1980). The dominant thermodynamic force for water absorption is site binding with discrete polar chains and peptide bonds (Breuer, Buras, & Fookson, 1980). A single layer of water molecules directly in contact with the surface is formed. This "chemisorption" occurs when bonds form between the adsorbed water and the surface of the wool molecules (D'Arcy & Watt, 1981).

The water adsorbed at low humidities associates with the polar groups of highest charge (eg. NH_3^+). The binding of water by amino groups occurs with an energy of binding higher than the energy needed for water to attach to other hydrophilic groups (Leeder & Watt, 1965). If more than one water molecule can associate with a charged group, the second and later molecules are adsorbed with less attractive force than the first molecule. Adsorption continues until the residual attractive forces at the charged site are balanced by the constraints imposed by the resistance of the molecular network to further swelling (Leeder & Watt). There

is a decrease in energy of binding of water to keratin with an increase in relative humidity; each increment of water reduces the average strength of attachment of water molecules already present in the wool (Leeder & Watt).

Chemisorption ceases when the absorbate (eg. water) can no longer make direct contact with the surface; it is therefore a single layer process. Multilayer physical adsorption occurs after the formation of a chemically adsorbed monolayer (D'Arcy & Watt, 1981). At higher water contents the major mechanism of adsorption is no longer association of water molecules with high energy sites.

Windle (1956) describes three types of water: 1) Water attached with the highest energy is localized water (bound water), the water hydrogen bonded at specific sites (to polar groups in the wool). 2) The next layer of water is attached to this localized water with hydrogen bonds of lower energy. 3) Loosely bound water analogous to liquid water is the third type of water bound in keratin. For water absorbed at high humidities, the water-keratin bonds are weaker than the water-water bonds.

Sakabe et al. (1987) used differential scanning calorimetry (DSC) to study the states of sorbed water on wool to determine the amount of bound water in wool fibres. They determined the amounts of three different kinds of water sorbed on wool fibres which are comparable to Windle's (1956) three types of water: non-freezing bound water, freezing bound water, and free water. Lynch and Webster (1979) using nuclear magnetic resonance (NMR) determined that there are three discrete mobile water phases in wool, the degree of mobility increasing as the water molecules are situated further from the binding sites of the wool molecules.

At present, no clear cut distinction can be made between bound water and mobile or condensed water; the relative properties of each vary with the moisture content of the system (Leeder & Watt, 1965). All bound water molecules are mobile (ie. they move from site to site) and are affected by relative humidity, although less so than liquid water (Maclaren and Milligan,1981, p. 303; Watt, 1980).

No portion of sorbed water is as mobile as liquid water. The average mobility of sorbed water increases at high relative humidity, with the formation of a hydrogen bonded network; however, at 80% relative humidity the mobility of some or all of the water molecules slowly decreases, possibly due to the inclusion of water in strong keratin-water-keratin bonds resulting in the formation of water bridges (Watt, 1980). Hydrogen bonding of water within a substrate (eg. wool) is weaker than that in liquid water but stronger than that in water vapor (Haly & Snaith, 1968; Watt). From data on heat of fusion of absorbed water in wool it has been determined that no water at water contents below 22.7% can have liquid-like structures (Haly & Snaith). At high relative humidity, water molecules prefer to associate with each other and tend to form small clusters (Watt); however, sorbed water molecules will not condense to a liquid water state.

Bound Water and the BET Monolayer

A portion of the total water content of wool is strongly bound to specific sites. An effective way of estimating the proportion of water bound to specific sites to the total water content of a system is the use of the Brunauer, Emmett and Teller (BET) equation (see Equation 7) (Karel, 1975; McLaren & Rowen, 1951). This equation is often used in the study of moisture sorption by wool (Morton & Hearle, 1975; Watt, 1980, Zeronian, 1984). The monolayer value (M_1) calculated from this equation is a measure of the water content at which a single layer or "monolayer" of water molecules is bound to the surface of the wool molecule.

The BET equation is stated as follows (Karel, 1975, p. 241):

$$a/M(1-a) = (1/M_1C) + [(C-1)/M_1C]\,a \qquad [7]$$

where: a= water activity
M= water content (moisture regain)
M_1= monolayer value (calculated)
C= constant (calculated)

This equation gives a sigmoidal isotherm which shows a good fit with several practical examples of absorption in the range of 5% to 50 % relative humidity (Morton & Hearle, 1975).

A plot of a/M(1-a) against a (Figure 7) should give a straight line from which the values of the constant, C, and M_1 can be determined (Karel; Morton & Hearle).

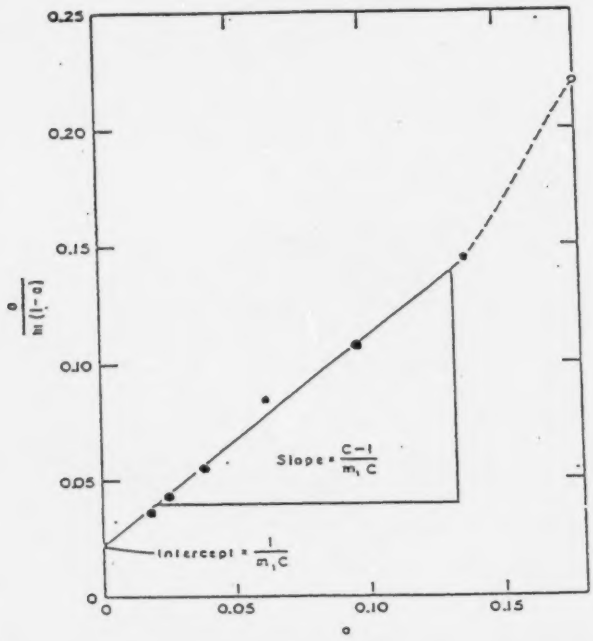

Figure 7. BET Plot

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The BET model assumes that there is localized sorption of strongly bound water which is in contact with a multilayer of liquid-like water on a free surface (Watt, 1980). The BET model considers that a number of monolayers are superimposed and at equilibrium there is a similar dynamic balance between rate of condensation and rate of evaporation from the monolayers (Watt). In order to maintain an equilibrium, the rate of condensation on a particular layer must equal the rate of evaporation from the adjacent layer.

The BET model has several drawbacks. It is generally applicable only in the region of relative humidity less than 50% and it assumes that all binding sites are identical (McLaren & Rowen, 1951). It neglects the interaction between neighbouring molecules in a layer and it takes

no account of effects due to swelling and mechanical constraint (Morton & Hearle, 1975; Windle, 1956). McLaren and Rowen warn against drawing too definite conclusions from the use of simple BET equations in the case of water sorption by proteins. Karel (1975), however, states that although the method is based on oversimplified assumptions, it is extremely useful as an estimate of the monolayer value.

D'Arcy and Watt (1981) and Windle (1956) are among some of the researchers who have attempted to improve the BET equation in order to obtain more accurate bound water content values for the wool-water system. These modified equations have been effective in improving the relationship between theoretical and observed isotherm values. Unfortunately, due to the increased complexity of these new equations, the modifications to the BET equation to correct its shortcomings destroy its simplicity, which is one of the more appealing qualities of this equation (van den Berg & Bruin, 1981).

Swelling of The Wool Fibre

Keratin swells on adsorption of water vapor over the entire humidity range (Watt, 1980). Wool fibres swell with the sorption of water molecules and may increase in diameter up to 18% (Alexander et al., 1963, p. 87; Maclaren & Milligan, 1981, p. 302). Breuer et al. (1980) found that wool fibres, with scales intact, increased in diameter by about 8-9% as the relative humidity of the ambient environment was increased from 0-93%.

During absorption, the wool fibre structure must expand to accommodate the water molecules in the intermolecular spaces (Alexander et al., p. 97; Breuer et al., 1980). There is a plasticizing action of the water molecules in pushing apart the molecular chains that permits more rapid transport of the sorbed water molecules (Watt, 1980). Breuer et al. (p. 322) state, for example, that "dry hair is a fairly rigid semi-crystalline porous solid. Water penetrates into the pores between various fibrils of the hair structure and pries them apart, thus bringing about a gradual increase of the hair volume". It is assumed that water molecules fill preexisting voids in the fibre (Breuer et al.), such as those in the cell membrane complex and the matrix.

The initial water sorbed, acting as a plasticizer, pushes apart crosslinks allowing more water to be sorbed and the fibre to swell (Breuer et al.). Reduced swelling above 20% relative humidity occurs and is partly due to filling of voids and partly due to immobilization of water molecules around charged groups in the protein (Watt).

The swelling of wool fibres with water is largely the result of swelling occurring in the matrix which makes amino groups accessible to more than one water molecule (Chapman, 1969; Leeder & Watt, 1965). The matrix becomes mechanically weaker with increasing water content (Watt, 1980). The matrix and intermediate filaments exhibit differential swelling properties due to the crystalline nature of the IFs (Watt). Spei (1984) found partial swelling in the intermediate filaments; however this swelling is not as great as that in the matrix.

Swelling can also occur between the cortical cells, in the cell membrane complex. A notable property of the intercellular cement is its ability to swell at high humidities. The low disulphide content of the intercellular cement, hence the lack of covalent crosslinks, confers ease of swelling and consequently ease of modification on fibre components (Leeder, 1986). The swollen structure at high humidities is much weaker than the less swollen fibre at low humidities. Swelling and weakening of the intercellular cement has been proposed as the mechanism by which fibres break down in formic acid (Leeder). It has also been noted that the swelling of the CMC forms channels allowing diffusion of molecules into the fibre (Leeder).

Capillary Pores

In fibre bundles, liquid water may be held by surface tension to the external surfaces of the fibres (Morton & Hearle, 1975, p. 236). For a tightly packed bundle of fibres the interstices should correspond to narrow capillaries and allow the condensation of liquid water (Watt, 1980). At high relative humidities, water will remain in larger capillaries between the fibres and the regain will increase (Morton & Hearle). Although capillary condensation may occur in the spaces between the fibres, the water cannot be considered as being condensed in capillaries

within the fibres (Watt, p. 219). The pores within the fibre are small and are not considered to be capillaries.

Freezing

Freezing of Water in Polymers

A temperature of 0°C is the equilibrium point where water freezes (forms ice crystals); however, ice will not necessarily form at this temperature (Boegh-Soerensen & Jul, 1985; de Quervain, 1975, p. 3). Ice will form at 0°C if there is an ice nucleus present, such as a crystal or dust particle, around which the crystal lattice may develop (de Quervain, p. 7). Both changes in temperature and the introduction of an ice nucleus perturb the water structure and alter the nature and extent of hydrogen bonding (LeMaguer, 1987). If there is no ice nucleus present, water may be supercooled to as low as -39°C before ice formation occurs (de Quervain, p. 8).

Ice is considered to be the solid phase of water (de Quervain, 1975, p. 3) which occurs as a three dimensional, hexagonal lattice of water molecules held by hydrogen bonds. Water has a higher density than ice because of this open crystal structure. When ice forms, there is a volume increase of 9% (Boegh-Soerensen & Jul, 1985, p. 53; de Quervain, p. 8) which can lead to a build up of stresses, cause a distortion of shapes and cracking of the surface of the material in which the ice is forming (Boegh-Soerensen & Jul). Due to the three dimensional structure and increased volume of ice vs. water, it is assumed that there are minimum space requirements within a material, such as a wool fibre, in order for ice crystals to form. Molecules have to be able to turn and rearrange before joining the open structure of the solid lattice. In general, at -40°C, a minimum of 200 water molecules must associate within a space of at least 4 nm (40 Å) in order for an ice crystal to initiate growth (Slade & Levine, 1991, p. 155). Water in capillaries less than 40 Å in radius is non-freezing (Slade & Levine, p. 129).

Fast cooling forms small ice crystals whereas slow cooling allows the formation of larger ice crystals (Boegh-Soerensen & Jul; Davies & Obafemi, 1985; Simatos & Turc, 1975) The size of ice crystals may change with prolonged storage, especially at temperatures near -18°C;

as well, temperature fluctuations during freezer storage lead to the growth of large ice crystals (Boegh-Soerensen & Jul). Ultra-quick freezing with liquid nitrogen (-196°C) can produce ice crystals as small as 5 nm (50 Å) in diameter (Rothmayr, 1975). This suggests that spaces of at least 5 nm (50 Å) are required for the smallest single ice crystals to form.

A fraction of the water in biological systems cannot be transformed into ice. Unfreezable water is often identified with bound water, those water molecules having close interactions with polymers and possessing properties very different from those of bulk water (Simatos & Turc, 1975). In narrow spaces such as capillary pores, the water layer in immediate contact with the pore wall has an ordered structure and reduced vapor pressure (de Quervain, 1975). In capillaries of 1 nm (10 Å) radius, water has a vapor pressure less than one third that of bulk water and a depressed freezing point of -15°C; such water can remain unfrozen indefinitely at freezing temperatures above -15°C (Slade and Levine, p. 129).

Water may still become immobilized in a rigid form at low temperatures even though ice crystals will not be formed. This water structure is amorphous and the water is considered to be in a "glassy" state, often referred to as vitreous water (de Quervain, 1975; Hoeve, 1980; Simatos & Turc, 1975). This water is usually classified as unfreezable water (Simatos & Turc).

Freezing point depends on the concentration of dissolved molecules in the water phase and not on the water content of a material (Boegh-Soerensen & Jul, 1985). The initial freezing point (the temperature at which ice begins to form) has to be used as the freezing temperature because the more the product is cooled below the initial freezing temperature, the more water will freeze out. This makes the remaining water phase more concentrated, and lowers the freezing point, requiring a progressively lower temperature to freeze the residual water (Boegh-Soerensen & Jul). The presence of solids (including mineral salts), sugars, alcohols, ketones, aldehydes and acids will generally impede crystallization and lead to amorphous rigid structures (eg. vitreous water) (Rey, 1975).

Slow cooling allows for strong electrolyte concentrations to develop (Simatos & Turc, 1975). As ice forms, solutes concentrate in the remaining liquid (Davies & Obafemi, 1985). The

concentration of salts and minerals leads to a change in pH, generally towards acidic (Boegh-Soerensen & Jul, 1985). Increased solute concentrations often increase chemical reactivity which may result in damage to lipid membranes, and denaturation of proteins in biological systems. Physico-chemical changes, such as loss of water binding capacity, increase with increasing solute concentration but may also decrease with cold temperatures (Boegh-Soerensen & Jul). In freezing, water is transformed into a nonactive component (LeMaguer, 1987), therefore, chemical and biological reactions cannot be supported by water in a frozen system.

Dielectric results for water absorbed in rigid polymers of collagen, elastin and methyl cellulose indicate that at room temperature the water molecules are mobile (Hoeve, 1980). Mobilization decreases at lower temperatures until collectively the water molecules become immobilized in a glassy state (Hoeve), the amorphous vitreous water described earlier. If at higher water contents sufficient polymer mobility exists, water diffuses out of the polymer interstices and forms ice as a separate phase while the polymer shrinks and forms irreversible bonds (eg. disulphide bonds, hydrogen bonds, ionic bonds) between molecules brought into contact by ice separation. Dehydration, therefore, can occur without net loss of hydrogen bonds (Hoeve).

Freezing is considered to be a gentle preservation method which will preserve to a great degree the initial cellular structure of a material (Boegh-Soerensen & Jul, 1985; LeMaguer, 1987). Freezing may be damaging, however, according to Hanafusa (cited in Davies & Obafemi, 1985), freezing and thawing may cause a partial unfolding of the helical structure of fibrous proteins. In microorganisms, bipolar relationships of membrane proteins and lipids change at sub-zero phase transition temperatures (Davies & Obafemi). In foods, freezing and thawing with no or a very short period of frozen storage has little effect on quality; most quality deterioration takes place during (freezer) storage (Boegh-Soerensen & Jul, 1985). Desiccation can occur during freezing and thawing as well as during freezer storage as water evaporates from unpackaged frozen foods. Moisture losses may vary from 0.5 to 2% and the degree of loss decreases with colder temperatures because colder air can contain less water

vapor (Boegh-Soerensen & Jul). Even if products are packaged, if the packaging does not fit tightly around the product, water will evaporate from the product and deposit on the inside of the package as frost (Boegh-Soerensen & Jul)

Freezing of Wool

Research regarding the freezing of wool fibres is limited. In discussing the freezing of proteins (eg. collagen), Hoeve (1980, p. 138) states that approximately 0.4 gram water/gram of protein form an unfrozen boundary layer at subzero temperatures. This bound layer has properties different from supercooled water and ice at the same temperature. Hoeve's findings also suggest that it is probable that the intermolecular spaces within the wool fibre are not large enough to accommodate ice crystal formation. Hoeve states that in narrow, fixed polymer interstices the space requirements are insufficient for the formation of three-dimensional ice crystals. For the cage-like ice structures to develop, cavities of several tens of angstrom (Å) units are required. The spaces in the matrix of wool cortical cells are 4 nm (40 Å), too small for the smallest possible, 5 nm (50 Å), ice crystals which result from ultra-quick freezing (Rothmayr, 1975). Ultra-quick freezing would not occur in practical situations.

Lynch and Webster's (1979) investigation of the freezing of water associated with wool keratin using nuclear magnetic resonance (NMR) found that at 235°K (-38°C) all freezable water in saturated wool was frozen; however, there was residual non-frozen water. They concluded that "it is unlikely that all the water sorbed in excess of 23% equilibrium water content freezes" (Lynch & Webster).

The study of Sakabe et al. (1987) using differential scanning calorimetry (DSC) to study the states of water sorbed on wool found that exothermic peaks on the DSC curves at -20°C and -35°C correspond to the freezing points of "free" and "freezing-bound water" respectively. Endothermic peaks at 0°C and -15°C correspond to the melting points of "free" and "freezing-bound water". At 33.5% water content, "non-freezing bound water" was determined to be 31.7% indicating that of the total amount of water sorbed and bound in the fibre at saturation, 31.7%

is not capable of freezing. They also found that water content must exceed 30% by weight to see identifiable endothermic and exothermic curves.

Ito, Sakabe, Miyamoto, and Inagaki (1984) examined the fibrillation of wool fibres after repeated freeze-thaw cycles. It was found that fibrillation as a result of repeated freeze-thaw cycles occurred only when 1) the outer cuticle of the fibre was removed, 2) the freezing rate was slow, and 3) the fibres were exposed to certain swelling media. No fibrillation occurred when water was the swelling media. For fibrillation to occur, it was necessary to weaken the intracellular cement with formic acid or dichloroacetic acid. The purpose of the study was to develop a method of separating the orthocortex and paracortex of the wool fibre so that each could separately be studied by amino acid analysis. The experiment was designed to provide extreme damage to the fibre structure. It was concluded that "freezing-thawing may be applied to separate the orthocortical and paracortical cells from the cortex entity without causing any serious damage to the cortical cells" (Ito et al.). The conclusion of Ito et al. implies that damage to the wool fibre as a result of freezing-thawing treatment occurred in the cell membrane complex between the cortical cells only after it was weakened with formic acid.

Freeze-Drying

Freeze-drying, also referred to as lyophilisation, is the result of the removal of water from a frozen material by sublimation. Water molecules move from solid ice to water vapor without passing through the liquid phase. Sublimation usually occurs at -20°C to -30°C and is accelerated by reduced pressure, although freeze-drying can occur at atmospheric pressure (Peacock, 1990; Rey, 1975).

In the freeze-drying process, the material being treated is frozen solid by low temperature cooling then dried by direct sublimation of the frozen solvents (eg. water), generally under partial vacuum (Rey, 1975). In drying, the interface between dry and frozen substances recedes from the surface to the interior of the frozen product and the evaporation rate decreases. The binding heat of water is much higher than the heat of sublimation; thus,

bound water is generally not removed and the remaining water is termed the "residual moisture" of the product (Rothmayr, 1975). The transformation of frozen solids into vapor is highly endothermic and requires a large amount of energy; therefore, freeze-drying processes often carefully add heat to the system (Rothmayr).

Freeze-drying is often used for the stabilization of materials. Materials that have been freeze-dried retain their shape and appearance as well as all their physical, chemical, and biological properties (Rey, 1975). The ice matrix within the frozen solid locks the histological structure of the materials in place and this structure is retained upon removal of water from the material. The structure of the frozen mass will be dependent on the way the material has been cooled and the temperature reached (Rey). The rate of freezing and pore size will determine the size of ice crystals. Large ice crystals result in a faster rate of sublimation due to better heat and mass transfer; however, large crystals may destroy the texture of materials (Rothmayr, 1975). Many freeze-dried materials may be reconstituted to their original shape and structure by the careful addition of moisture (Rey).

Freeze-Drying in Artifact Conservation

Peacock (1990) reports that freeze-drying is commonly used for the drying of wet organic archaeological materials such as wood and leather. Application of the process to textiles has been limited; however, research into the use of freeze drying in textile conservation is currently in progress (Peacock). Jakes and Mitchell (1992) found vacuum freeze-drying to be disruptive to fabric and fibre structures.

The freeze-drying process is usually applied to materials recovered from wet-frozen, frozen-terrestrial, or marine archaeological sites. Its use on wood and leather is popular due to the success of the procedure in maintaining the structure of the materials. Air drying has usually resulted in the collapse of the structure of wood and leather, whereas air drying has, for the most part, been successful with textiles.

Peacock (1990) outlines the common freeze-drying procedure used in artifact conservation; objects are processed as follows:

1. wet storage at cool temperatures (≈ 0°C) and treatment with a biocide, or frozen storage,
2. wet cleaning with mechanical or possibly chemical cleaning,
3. pre-treatment with protectants such as consolidants or plasticizers,
4. pre-freezing,
5. freeze-drying,
6. reintroduce dried material to normal atmospheres.

In northern archaeological sites where materials are frozen for most of the year, objects exposed to the atmosphere may be naturally freeze-dried (Peacock, 1990). Wind increases the movement of air across the surface of an exposed artifact and aids in the removal of moisture from the material. The low bulk and large surface area of textiles makes ice within their structures readily accessible to sublimation through freeze-drying (Jakes & Mitchell, 1992).

Freezing Used as a Method of Slow-Drying Waterlogged Textiles

Jakes and Mitchell (1992) evaluated the effectiveness of freezing as a method of slowly drying waterlogged textiles. Wet textiles were laid flat on screens and placed in freezers at approximately -28°C; an air current of 5 mph in the freezer created a wind chill resulting in an effective temperature of approximately -37°C. These conditions, combined with the low relative humidity within the freezer, allowed for sublimation of ice from the exposed frozen textiles and their subsequent drying. The textiles were dry when removed from the freezer after two months (Jakes & Mitchell). Based on visual evaluation of the fibres and fabrics using SEM, it was concluded that the slow drying of textiles while frozen appeared to be a less disruptive method of drying and preservation than vacuum freeze-drying (Jakes & Mitchell).

Freezing as a Means of Insect Eradication

In museums, the freezing of artifacts as a method of killing insects is gaining popularity over the use of chemical insecticides ("To Freeze," 1991). Several researchers have found that mortality of all stages of insect life (eg. eggs, larva, adult) has been successfully achieved with

methods where the artifacts are frozen to temperatures below -20°C (Florian, 1986; Gilberg & Brokerhof, 1991).

Florian's (1986) method is commonly used in the museum community ("To Freeze,", 1991; Wolf, 1992). This method calls for sealing the artifact in polyethylene and removing as much air from the package as possible. Removal of air is recommended to reduce the possibility of water vapor in the bag condensing on the artifact (Florian). The artifact is to be frozen for a minimum of 48 hours at a temperature no higher than -20°C. Freezing is followed by slow thawing of the artifact, and then refreezing under the same conditions. The rate of thawing suggested by Florian is a return to 0°C over 8 hours. This method has been found to successfully kill larvae and eggs of several common museum pests (Florian). To date research into how this method affects the material being frozen has not been reported.

CHAPTER 3 MATERIALS AND METHODS

Yarns

Skeins of new, unbleached wool yarn were used in this research project. Experiments were done on new wool rather than naturally aged wool in order to reduce variability in the wool which may be caused by previous unknown degrading factors such as light, oxygen, microorganisms, and cleaning agents. Unbleached wool yarn was desirable in order to reduce the effects of prior chemical treatments.

The yarn was purchased locally from "The Real Wool Shop" in Stony Plain, Alberta. Briggs & Little Woolen Mills in Harvey Station, New Brunswick is the mill which had processed the yarns. The skeins were labelled "100% pure wool, 113 g, 2 ply, No. 2/12, lot no. 24". The yarn had a linear density of ≈530 tex and contained a mixture of fibres from various fine-hair breeds of sheep (J. Little, personal communication, March 16, 1992). Six 113 g skeins from the same lot were purchased. Five of these skeins were used in the testing.

The wool had not been subjected to bleaching, dyeing, or carbonizing treatments (J. Little, personal communication, March 16, 1992). The fleece had been scoured to remove the lanolin prior to carding and spinning. A synthetic oil had been added to the wool to facilitate ease of spinning. The yarns were spun to 2-ply using a woolen system. Because the fleece had not been carbonized, small pieces of vegetal matter (eg. grass or straw) were occasionally found in the spun yarns.

Due to the greasy nature of the yarns, the five skeins of yarn were cleaned to remove any residual processing contaminants and added spinning oils. Cleaning also served to remove much of the loose vegetal matter in the yarns. The yarns were commercially dry-cleaned at low heat for 3 minutes in freshly distilled perchloroethylene by Delton All Fashion Cleaners in Edmonton. The yarns were then carefully wet-cleaned in a 0.2% w/v solution of SHUR-GAIN® anionic detergent in distilled water at 21.5°C. The yarns were rinsed thoroughly by immersing in five separate distilled water baths (approx. 5 minutes/rinse). After washing, the yarns

were blotted with a cotton terry towel and laid flat to air dry. Prior to sampling, the dry yarns were pre-conditioned at 50°C for two hours, then conditioned for at least 24 hours at 65 ± 2% RH and 20 ± 2°C, standard textile testing conditions (CAN/CGSB-4.2 No. 2-M88).

Sampling Procedure

For greater ease of handling, yarn specimens were pre-cut to the appropriate specimen sizes for each of the analytical tests to be performed. Table 3 summarizes the size and number of specimens required for the various tests on yarns exposed to each freezing treatment.

Table 3
Number and Size of Specimens of Wool Yarns Cut for Testing

Test	No. of specimens/test/freezing treatment	Size of specimen
Tensile properties	30 (+ 5 trial specimens)	400 mm
Moisture absorption properties	18	1.89 m (≈ 1 g)
Chemical solubility	2	0.19 m (≈ 100 mg)
Microscopic appearance	not pre-cut	10 mm, specimens to be taken from the unused tensile testing specimens

Specimens were cut from the entire length, except for the first and last metre, of each of the five clean skeins of yarn. No more than 10 specimens were cut consecutively from the same skein. Skeins were randomly rotated throughout the specimen cutting process. After cutting, specimens were randomly assigned to groups corresponding to each of the freezing and conditioning treatments as shown in Table 4. Two groups of pre-cut yarns, one containing *dry* wool (Treatment Group 15), the other containing *wet* wool (Treatment Group 16) were identified, dated and placed in the freezer for an indefinite period. Analysis of the long term effects of continuous freezer storage will be possible at a later date.

Table 4
Treatment Variables: Nature and Length of Freezing Cycle and Moisture Content of Specimens

Treatment Group	Conditioning Treatment		Freezing Type and Length of Treatment (days)		
	Dry	Wet	No Freezing	Freeze-Thaw	Continuous Freezing
1	x		0		
2		x	0		
3	x			20	
4	x			40	
5	x			60	
6	x				20
7	x				40
8	x				60
9		x		20	
10		x		40	
11		x		60	
12		x			20
13		x			40
14		x			60
15	x				indefinite
16		x			indefinite

Conditioning of Wool

"Dry" yarns were conditioned at 65 ± 2% RH, and 20 ± 2°C (CAN/CGSB-4.2 No. 2-M88). These conditions are standard textile testing conditions and are easy to control and to replicate. "Wet" yarns were wet-out by immersing in room temperature (20°C) distilled water for one hour. The yarns were then gently blotted for approximately 10 seconds with a cotton terry towel to reduce excess water in each set of yarns. The dry and wet conditioned yarns were sealed in polyethylene freezer storage bags (Ziploc®-brand) and as much air as possible was

evacuated from the bags before sealing. This was accomplished by gently sucking the air out through a plastic drinking straw.

Freezing Treatments

The new wool yarns, dry and wet, were each exposed to either cyclical or continuous freezing. Freezing took place in a home chest freezer without frost free cycling (W.C. Wood Model OC42-4C, 418 L capacity). The freezing temperature averaged -25°C (*SD* 1.4) as determined by twice daily monitoring, over 60 days, with a low temperature thermometer (Fisher Scientific, Cat. No. 15-038). The -25°C temperature allowed for minor fluctuations in temperature to occur while maintaining freezing conditions below Florian's (1986) recommended -20°C temperature. The bags containing the wool were spaced throughout the freezer in three wire baskets which were rotated between three positions once a day to allow consistent, even exposure to the cold atmosphere.

Freezing and Thawing Cycles

The total length of one freezing and thawing cycle was 24 hours. The bags containing the wool yarns were placed in the freezer at -25°C and allowed to equilibrate for 16 hours, then removed from the freezer and thawed at room temperature for 8 hours in a controlled temperature (20 ± 2°C) conditioning room. The wool yarns remained in the sealed polyethylene bags throughout the freezing and thawing treatment. Yarn specimens were withdrawn for evaluation of physical and chemical properties after 20, 40 and 60 cycles.

Continuous Freezing

For continuous freezing, the bags of wool yarns were placed in the freezer set at -25°C where they remained for 20, 40, and 60 days with no thawing until they were removed from the freezer after completion of the freezing period. The withdrawal times of the continuously frozen yarns corresponded with the final withdrawal times for the yarns exposed to cyclical

freezing. The wool yarns remained in the sealed polyethylene bags during thawing in the controlled temperature conditioning room which was at 20 ± 2°C.

Conditioning After Freezing

All of the wool yarns were tested after preconditioning and conditioning according to Canadian Standard Test Method CAN/CGSB-4.2 No.2-M88 "Conditioning Textile Materials for Testing". Once the bags of wool had been removed from the freezer at the end of each freezing treatment, they remained sealed, at room temperature, in the conditioning room (20 ± 2°C) for 24 hours. This was to ensure that the temperature of the bags was equilibrated with that of the surrounding environment so that condensation of moisture from the conditioning room onto the wool specimens was avoided. After the 24 hour equilibration period, the yarns were removed from the bags, laid flat on cotton terry towels, and allowed to air dry in the conditioning room (65 ± 2% RH and 20 ± 2°C) for 24 hours. The yarns were then preconditioned at 50°C for 2 hours and conditioned at 65 ± 2% RH and 20 ± 2°C for 24 hours before testing (CAN/CGSB-4.2 No. 2-M88).

Analytical Test Methods

Changes in the wool were monitored by physical and chemical tests. Physical tests were performed to evaluate tensile properties. Due to the limited sensitivity of tensile testing (Maclaren & Milligan, 1981), additional tests were selected to help determine smaller degrees of change in the test specimens. Moisture sorption isotherms were determined and chemical tests were used to detect changes at the molecular level. As well, scanning electron microscope (SEM) analysis of fibre appearance was performed.

Tensile Testing

Tensile tests on yarns were used to determine changes in breaking strength, extension at break, and energy at break which may indicate changes in the fibre structure. The tensile tests

on 30 yarn specimens per treatment group were conducted as prescribed by the Canadian standard test method CAN/CGSB-4.2 No 9.4, "Breaking Strength of Yarns - Single Strand Method". Specimens measuring 400 mm in length were tested. The testing was carried out under standard conditions of 65 ± 2% RH and 20 ± 2°C. An Instron Universal Testing Instrument, Model 4202, with Instron series 2714 pneumatic cord and yarn grips, was used for the tensile tests. The Instron was equipped with a 50 kgf load cell with the load range was set at 0-5 kgf. The gauge length (initial yarn length) was 125 mm. The cross-head speed was 220 mm/min for all tests so that the average time to break was within the required 20 ± 3 seconds.

Extension at break was tested concurrently with tensile strength and is the elongation or change in length (ΔL) of the specimen at break expressed as a percentage of the original length (L_o):

$$\text{extension (\%)} = 100\ \Delta L\ /L_o \qquad [8]$$

Energy at break (Joules), or the work of rupture was also recorded. This is the energy required to break the specimen (a measure of toughness), and can be determined by calculating the area under the load-elongation curve.

Moisture Vapor Sorption Isotherm Determination

Determination of moisture vapor sorption isotherms for specimens before treatment and after 20, 40, and 60 days of freezing and thawing cycles and continuous freezing was used to evaluate changes in the sorption behavior of the wool yarns.

Methods for the determination of sorption isotherms using saturated salt solutions have been described in the literature (Karel, 1975; Speiss and Wolf, 1987; Zeronian, 1984). A procedure based on the methods of Karel and Zeronian was used. The six saturated salt solutions shown in Table 5 were used to produce relative humidities ranging from 11% to 97% in closed containers at room temperature. (In the closed container, a saturated solution of $NaNO_2$, for example, produces a relative humidity of 65% in the air above the solution at 20°C.) The moisture regain of wool specimens at each of the six relative humidities was determined.

These regain values were used to construct moisture sorption isotherms for the wool yarns exposed to each of the conditioning and freezing treatments.

Table 5
Saturated Salt Solutions used to Maintain Constant Relative Humidity

salt	approximate RH at 20°C	mass of salt used	volume of hot distilled water used
$LiCl \cdot H_20$	11%	125 g	150 mL
$MgCl_2 \cdot 6H_2O$	32%	355 g	100 mL
$Mg(NO_3)_2$	53%	275 g	100 mL
$NaNO_2$	65%	165 g	200 mL
NaCl	75%	65 g	200 mL
K_2SO_4	97%	35 g	200 mL

Adapted from Speiss and Wolf (1987)and Zeronian (1984).

Each of the salt solutions was prepared in a glass desiccator (Fisher Scientific, Cat. No. 08-632 or 08-595C) which was used as the humidity chamber. A seal between the cover and the jar was required to ensure a constant environment. This seal was maintained by applying a thin coating of vacuum grease to the flanges of the lid and jar, pressing the lid onto the jar, and turning the lid at least 180°. The desiccators were kept at a mean temperature of 20 ± 2°C in the controlled temperature conditioning room in order to maintain a constant temperature throughout the testing period. The salt solutions were stirred with a glass rod daily for one week prior to use in order to ensure maximum dissolution of the salts.

Three separate yarns from each group of yarns exposed to each of the freezing treatments were assigned to one of the six relative humidity chambers for moisture regain determination. Each specimen was exposed to only one relative humidity chamber.

Aluminum weighing dishes (approx. 1 g each) were dried to constant mass at 105°C in a Fisher, forced draft, Isotemp® oven (Model 13-244-2). One gram of wool yarn was loosely coiled on itself, placed in the aluminum weighing dish and dried to a constant mass at 105°C. Specimens were cooled for 1 hour over Drierite® desiccant before weighing on a Mettler

analytical balance. A mass was considered to be constant when two consecutive weighings differed by no more than 0.5 mg. The average of these two masses was used to calculate the dry mass (M1).

Once the dry mass of a yarn had been determined, it was placed in one of the humidity chambers and allowed to equilibrate for 4 days before weighing on a Sartorius analytical balance. The conditioned mass (M2) was the average of three consecutive masses which differed by no more than 0.5 mg. This procedure was modified for the specimens from the 97% relative humidity chamber; the test specimens rapidly lost moisture upon removal from the chamber and it was difficult to obtain three consecutive masses differing by no more than 0.5mg. Specimens were left undisturbed in the 97% RH chamber for 4 days then weighed at 9:00 am for three consecutive days thereafter and the masses averaged for M2.

The moisture regain for each yarn was then determined as follows:

$$\text{regain } (\%) = 100\,(M2-M1)/M1$$

where: M1 = mass of dry specimen
M2 = mass of conditioned specimen [10]

The moisture regain value at each level of relative humidity is the average of values obtained from three yarns per freezing treatment. An isotherm of the relative humidity vs. mean moisture regain was plotted for the yarns exposed to each combined conditioning and freezing treatment.

BET Monolayer Value Determination

Using the simple linear ($y = a + bx$) relationship of Equation 7 shown below, a BET plot was made for the wool yarns exposed to each freezing treatment in order to determine M_1, the moisture content at which a monolayer of water molecules is formed within the wool fibres.

$$a/M(1-a) = (1/M_1C) + [(C-1)/M_1C]\,a \qquad [7]$$

where: a = water activity
M = water content (moisture regain)
M_1 = monolayer value (calculated)
C = constant (calculated) (Karel, 1975, p. 241)

It is only in the range of 0%-50% RH that the slope of the isotherm is linear and the BET equation is applicable. Moisture regain values at 11%, 32%, and 53% were used for **M**. Water activity (**a**) was taken as RH/100. The values for **a** were plotted against **a/M(1-a)** and a straight line was fitted to the points of the isotherm. From the BET equation where the y-intercept equals $1/M_1C$, and the slope of the line equals $[(C-1)/(M_1C)]$, the two unknowns, **C** and M_1 were calculated. Examples of a typical plot and calculations are given in Appendix A-1.

For each set of yarns exposed to the various conditioning and freezing treatment combinations, three BET monolayer values (M_1) were calculated, one per experimental replication, using the moisture regain values at 11%, 32% and 53% RH, then an average value was calculated.

Tributylphosphine-Alcoholic Sodium Iodide Solubility Testing

A solubility test was used to determine whether changes had occurred at the molecular level as a result of freezing treatments. The tributylphosphine-alcoholic sodium iodide (TASI) solubility test (Kilpatrick & Maclaren, 1970) was chosen because of its relative sensitivity and simplicity.

The alcoholic sodium iodide solvent was prepared according to the procedure of Kilpatrick and Maclaren (1970). Sodium iodide (375 g) was completely dissolved in 125 mL of ethanol in a 500 mL volumetric flask, then the volume was made up to 500 mL with distilled water. The solvent was then transferred to a clean reagent bottle for easier storage and handling. The ethanolic sodium iodide solvent has an indefinite shelf life (Kilpatrick and Maclaren); therefore, enough solvent for all of the tests to be run was prepared at once.

The test was carried out by weighing approximately 100 mg of wool yarn, conditioned at 65 ± 2% RH and 20 ± 2°C, into a tared 50 mL conical flask. Ethanolic sodium iodide solution, 10 mL, was added to the flask with a 10 mL pipette. Three drops of tributylphosphine were added, the flask was stoppered and shaken for 24 hours using a Burrel wrist-action shaker, model 75, set at level 2 for gentle shaking. After shaking, the residue was filtered through a

tared sintered-glass Büchner funnel of "porosity 2" (70 - 100 µm pore size) using a tap aspirator vacuum. The filtered residue was washed with 4 x 100 mL of distilled water, then rinsed with 2 x 25 mL of acetone. The residue and funnel were dried at 50°C for 4 hours, then conditioned at 65 ± 2% relative humidity and 20 ± 2°C for 24 hours. Constant conditioned weights were determined and the solubility was calculated as follows:

$$\text{solubility (\%)} = 100\,(M1-M2)/M1$$

where: M1 = mass of wool before treatment
M2 = mass of residue [11]

Two yarn specimens from each set of yarns exposed to the various conditioning and freezing treatments were tested using this method and mean solubility was reported.

Scanning Electron Microscopy (SEM) Analysis

SEM analysis was used for qualitative evaluation of the fibre appearance after freezing treatment. The dry unfrozen yarns and the yarns frozen cyclically or continuously while dry or while wet for 60 days were examined using the scanning electron microscope and evaluated for changes.

A piece of yarn was unravelled and several fibres, cut to approximately 0.5 cm in length, were mounted across a stub with double-sided adhesive tape. Conductive carbon glue was applied to the ends of the fibres to increase the conductivity through the stub. The specimens were then sputter-coated with 15 nm of gold to provide a conductive surface, and viewed under various magnifications using a Cambridge Stereoscan 250 scanning electron microscope. Photographs were taken at magnifications of 130x, 720x, 1300x, and 3500x.

Statistical Analysis of Data

A two-way analysis of variance (ANOVA) was performed on the data for each dependent variable to determine which main effects and interactions were statistically significant. The experimental variables are summarized in Table 6. The freezing treatment

variable included both the type of freezing performed, cyclical or continuous, and the length of each treatment.

Table 6
Summary of Experimental Variables

Dependent Variables	Independent Variables	
	Factors	Levels
yarn tensile strength	Conditioning Treatment:	dry
extension at break of yarns		wet
energy to break yarns		
moisture regain at 11% RH	Freezing Treatment:	no freezing
moisture regain at 32% RH		20 freeze-thaw
moisture regain at 53% RH		20 continuous
moisture regain at 65% RH		40 freeze-thaw
moisture regain at 75% RH		40 continuous
moisture regain at 97% RH		60 freeze-thaw
BET monolayer value		60 continuous
Tributylphosphine-alcoholic sodium iodide solubility		

The UANOVA procedure available through the SPSS-X, Release 3.0, statistical program on the University of Alberta mainframe computer was used for statistical analyses of the test results. F-tables summarizing the significance of main effects and of interaction effects are found in Appendix A-2.

After the two-way ANOVA was carried out, and the significance of main effects and interactions determined from the F-Tables, multiple comparisons of treatment group means were performed to determine where there were significant differences between groups. Duncan's Multiple Range Test (α=0.05) and Scheffé's Test (α=0.05) were used for the multiple comparisons of means. Scheffé's Test is a very stringent test at α=0.05 and was used to reduce

the occurance of Type I errors, or reduce the number of inexplicable significantly different means identified by Duncan's Multiple Range Test.

Comparisons on the basis of the significance of interaction effects took precedence when multiple comparisons of treatment groups were carried out. Bowerman and O'Connell (1990) suggest that if there is significant interaction, it is not reasonable to test the effects of individual factors. In the cases where the conditioning and freezing treatments significantly interacted, multiple comparisons were made between each of the means from the 14 total treatment combinations.

If interaction was not significant, means were compared on the basis of the main effects which were determined to be significant. Milliken and Johnson (1984) suggest that if the two factors (eg. conditioning and freezing) do not significantly interact, then the effects of each factor can best be compared after averaging over the effects of the second factor, because, averaging gives the shortest possible confidence intervals on effect differences. Therefore, comparisons of the effects of type of freezing were made on the average of the total number of specimens exposed to that freezing treatment, an average of both the wet and dry yarns; and the effects of conditioning treatment were compared on all of the yarns exposed to that conditioning treatment without consideration of the freezing treatment.

CHAPTER 4 RESULTS AND DISCUSSION

The purpose of this study was to determine if changes in wool yarns resulted from freezing treatments. In order to evaluate the effects of various freezing treatments on new wool yarns, changes in physical and chemical properties were investigated. The physical properties included tensile strength, extension at break, energy at break and moisture sorption. Chemical solubility was used to detect changes at the molecular level. Wool fibres were examined with a scanning electron microscope (SEM) to determine whether changes in fibre surface appearance had occurred.

Tensile Properties

Tensile tests were used to determine changes in tensile breaking strength, extension at break, and energy at break of wool yarns which were dry or wet while exposed to cyclical or continuous freezing for up to 60 days. Raw data from the tensile tests are presented in Appendix A-3. The raw data were analyzed by a two-way ANOVA procedure. Multiple comparisons of means based on the significant effects were made using Duncan's Multiple Range Test (α=0.05).

It was determined that there were no significant interactions between the effects of the two independent variables of conditioning treatment (dry or wet) and freezing treatment (cyclical or continuous for 0, 20, 40, or 60 days) on the tensile strength, extension at break, and energy at break of the wool yarns. The individual factors did, however, have significant effects on the means of the samples exposed to the various levels of each. The condition of the wool had a significant effect on the tensile strength and extension at break of the yarns. The freezing treatment had a significant effect on the tensile strength, extension at break, and energy at break of the wool yarns. Table 7 summarizes the tensile testing results in terms of the freezing treatment effects. Based on the suggestions of Milliken and Johnson (1984) regarding comparisons of main effects, the mean values reported and compared for each freezing

Table 7

Tensile Strength, Extension at Break, and Energy at Break of Wool Yarns Exposed to Continuous Freezing or Multiple Freeze-Thaw Cycles Regardless of Condition (dry or wet) During Freezing.

	Tensile Strength		Extension at Break		Energy at Break	
Freezing Treatment	mean (N)	% change	mean (%)	% change	mean (J)	% change
No Freezing	$20.3_{a,b}$		$56.3_{a,b}$		0.741_{a}	
Freeze-Thaw (cycles)						
20	$20.3_{a,b}$	0	$58.5_{c,d}$	+3.9*	$0.774_{a,b}$	+4.5
40	$20.5_{a,b}$	+1.0	55.8_{b}	-0.9	0.744_{a}	+0.4
60	$20.5_{a,b}$	+1.0	$58.1_{a,c,d}$	+3.2	$0.778_{a,b}$	+5.0
Continuous Freeze (days)						
20	19.9_{a}	-2.0	$57.0_{a,b,d}$	+1.2	0.725_{a}	-2.2
40	20.7_{b}	+2.0	55.3_{b}	-1.8	0.752_{a}	+1.5
60	20.9_{b}	+3.0	59.1_{c}	+5.0*	0.804_{b}	+8.5*

Note 1. Mean of n=60 yarns (sum of the dry and wet yarns) from each freezing treatment for tensile strength, extension at break, and energy at break.

Note 2. % change when compared to the unfrozen control.

Note 3. Means indicated with the same subscript (within each column) are not significantly different at α=0.05 as determined by Duncan's Multiple Range Test (α=0.05)

* statistically significant change

treatment are for all of the yarns, whether in a dry or wet condition, which were exposed to that freezing treatment (n=60).

Yarn Tensile Strength

Tensile breaking strength results would indicate damage to the textile fibres (chain scission, changes in intermolecular bonds) if the yarns exposed to freezing were significantly weaker than the control specimens. Figure 8 illustrates the mean tensile strength (N) of wool yarns after 0, 20, 40, and 60 days of cyclical or continuous freezing while in a dry or wet state. The change in tensile strength of wool yarns frozen cyclically or continuously for up to 60 days, regardless of dry or wet condition, compared to the unfrozen control ranged from a 2% decrease to a 3% increase as shown in Table 7. These changes from the original were not found to be significant, thus the exposure of wool yarns to freezing conditions for up to 60 days did not affect their tensile strength.

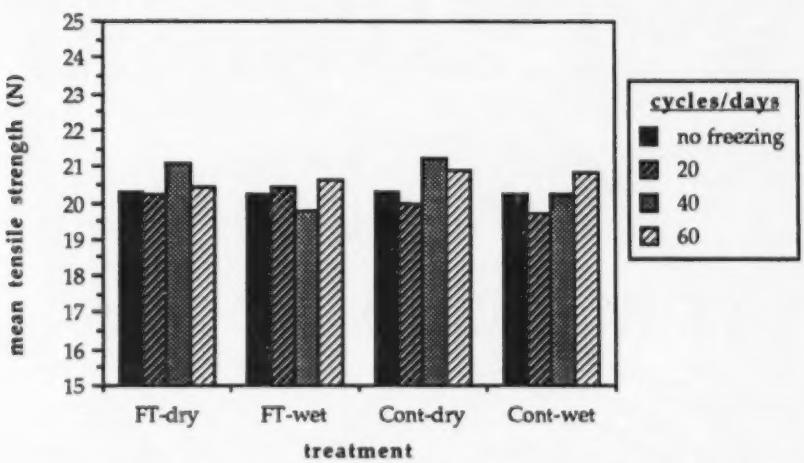

Figure 8: Tensile strength of wool yarns exposed to dry or wet conditions and freezing treatments.

Significant differences in tensile strength of the wool yarns exposed to the 7 different freezing treatments, regardless of dry or wet condition (n=60) were identified. Table 7 lists the mean tensile strength of wool yarns exposed to each of the cyclical and continuous freezing

treatments and indicates where significant differences between freezing treatments exist. The tensile strength of the wool yarns continuously frozen for 20 days (19.9 N) was found to be significantly lower than the tensile strength of the wool yarns continuously frozen for 40 days (20.7 N) and for 60 days (20.9 N). The tensile strength results of the yarns exposed to each of these three continuous freezing treatments were not found to be significantly different from those of the wool yarns exposed to the other freezing treatments. There is no explanation for the lower strength after 20 days of continuous freezing, further investigation is required.

The mean tensile strength of the wool yarns which were wet, regardless of length or type of freezing treatment, was 20.2 N (n=210) after drying and reconditioning, whereas the dry yarns had a tensile strength of 20.6 N (n=210). While the wool exposed to wet conditions was only 2% weaker than the wool which was dry, the strength loss of the wool yarns after wetting, without the interaction of freezing treatment, was statistically significant. It is possible that swelling of the fibre as a result of sorption of water may have caused some permanent rearrangement of molecules or reformation of intermolecular bonds within the fibres, resulting in the slightly reduced tensile strength after exposure to wet conditions.

In summary, the results of tensile strength testing of wool yarns indicate that when wool is frozen, cyclically or continuously, for up to 60 days there are no significant changes in tensile strength regardless of condition (dry or wet). These results suggest that molecular bonds are not broken by the freezing and thawing or continuous freezing procedures. Because the changes in tensile strength after 60 days of freezing were small and not found to be statistically significant, an extended period of freezing, longer than 60 days, is necessary to determine if there would be a significant change in strength if wool yarns are exposed to long-term freezing. The freeze-thaw treatment used to kill insects should not be damaging to wool textiles.

Extension at Break

Changes in extension at break were used to estimate whether inter- and intra-molecular bond changes had occurred. Extension at break was calculated from the elongation at break

measurements for each yarn tested using Equation 8 (Extension (%) = 100 ΔL/Lo). Figure 9 illustrates the mean extension at break (%) of wool yarns after 0, 20, 40, and 60 days of cyclical or continuous freezing while in a dry or wet state. The change in extension at break of wool yarns frozen cyclically or continuously for up to 60 days, regardless of dry or wet condition, compared to the unfrozen control ranged from a 1.8% decrease to a 5.0% increase as shown in Table 7. Only the wool yarns exposed to 20 freeze-thaw cycles and those exposed to 60 days of continuous freezing showed significant increases in extension of 3.9% and 5.0%, respectively.

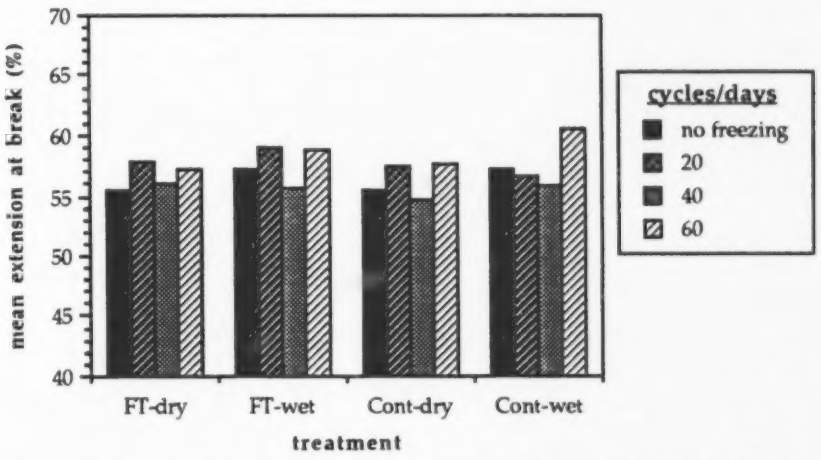

Figure 9: Extension at break of wool yarns exposed to dry or wet conditions and freezing treatments.

Significant differences in mean extension at break of the wool yarns exposed to the 7 different freezing treatments, regardless of dry or wet condition (n=60), were identified. Table 7 lists the mean extension at break of wool yarns exposed to each of the cyclical and continuous freezing treatments and indicates where significant differences between freezing treatments exist. Whether the wool was continuously frozen or frozen and thawed repeatedly, there were no significant differences in extension at break for those samples exposed to the same length of freezing (0, 20, 40, or 60 cycles/days). Comparisons of treatment group means indicated that the samples exposed to 20 freeze-thaw cycles and to 60 days of continuous freezing showed significant differences when compared to several other treatment groups. The

extension at break of wool yarns after 60 days of continuous freezing (59.1%) was found to be significantly higher than the extension after 20 days (57.0%) and 40 days (55.3%) of continuous freezing. The increase in extension at break after 20 freeze-thaw cycles does not continue as the length of the cyclical freezing treatment increases. Neither is there a consistent increase in extension at break up to 60 days of continuous freezing. The difference in extension at break after 20 freeze-thaw cycles cannot be explained without further testing. It would be expected that the increase would continue as the length of freezing treatment increased if there was a change within the fibre's molecular structure; this did not occur.

The tensile strength results suggest that the extension at break of wool which was wet may also be different from that of the dry wool. Wet wool fibres may experience swelling and subsequent rearrangement of molecules and intermolecular bonds. It is possible that these rearrangements, if permanent, could increase the extension at break of the wool yarns. The mean extension at break of the wool yarns which were wet, regardless of freezing treatment, was 57.7% (n=210) after drying and reconditioning, whereas the dry yarns (n=210) had an extension at break of 56.6%. Although the wool yarns exposed to wet conditions had only a 2% higher extension than the wool which was dry, this increase in extension after wetting, without the interaction of freezing treatment, was statistically significant.

In summary, there were few significant differences in extension at break between treatment group means when wool yarns were subjected to freeze-thaw cycles or continuous freezing for up to 60 days. After 60 days of continuous freezing there was a significant increase in extension at break. An increase in extension suggests that several things may have occurred. When a stress is applied to a fibre, there is a straightening of the fibre itself (removal of crimp), then a straightening of molecular chains in the amorphous regions, followed by breakage of intermolecular bonds and finally, failure in the main molecular chains. The spaces in the wool fibres are not large enough to accommodate ice crystals (Alexander, Hudson, & Earland, 1963; Rothmayr, 1975) which might physically break molecular bonds. However, after 60 days of freezing, it is possible that moisture present in the fibres could cause sufficient

swelling to rearrange molecules or alter intermolecular bonds resulting in an increase in breaking extension.

Energy at Break

Energy at break, or work of rupture, is a measure of the overall toughness of a fibre, taking both breaking strength and extension at break into account. It is a measure of the amount of energy required to stretch a fibre or yarn to the breaking point and is determined by calculating the area under the stress-strain curve. Both changes in the tensile strength and the elongation at break can affect the energy to break. Figure 10 illustrates the mean energy at break (J) of wool yarns after 0, 20, 40, and 60 days of cyclical or continuous freezing while in a dry or wet state. The change in energy to break the wool yarns after freezing ranged from a 2.2% decrease to an 8.5% increase as shown in Table 7. The 8.5% increase after 60 days of continuous freezing was the only significant change from the unfrozen control. This increase is primarily due to the increase in area under the stress-strain curve as a result of the significant increase in extension at break after 60 days of continuous freezing.

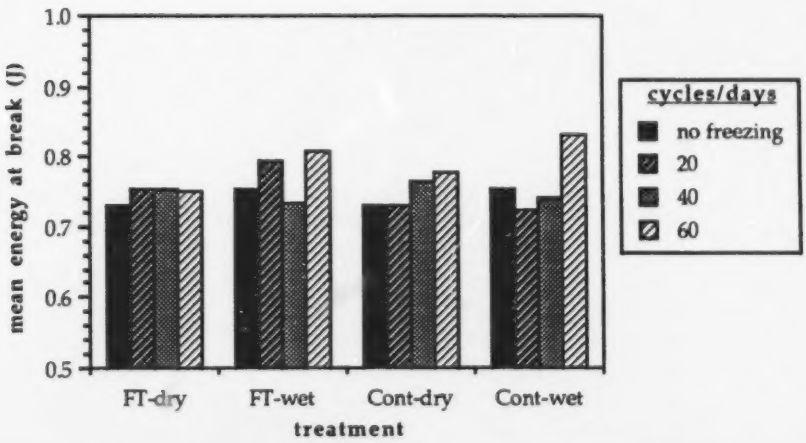

Figure 10: Energy at break of wool yarns exposed to dry or wet conditions and freezing treatments.

Significant differences in the energy to break the wool yarns exposed to the 7 different freezing treatments, regardless of dry or wet condition (n=60), were identified. Table 7 lists the mean energy at break for wool yarns exposed to each of the cyclical and continuous freezing treatments and indicates where significant differences between freezing treatments exist. All of the significantly different pairs of treatment means identified include the wool yarns exposed to 60 days of continuous freezing. The mean energy at break after 60 days of continuous freezing (0.804 J) was found to be significantly higher than the mean energy to break for the unfrozen yarns (0.741 J), the yarns frozen continuously for 20 days (0.725 J), and those frozen continuously for 40 days (0.752 J). This same relationship occurs with the extension at break results. Therefore, the differences in energy at break between the continuously frozen yarns are a result of the significant differences in extension at break. Changes in the energy to break the yarns exposed to cyclical freezing were not significant.

There were no significant effects due to the conditioning treatment (wet vs. dry). This means that, regardless of freezing treatment (cyclical or continuous for 0, 20, 40, or 60 days), there is no difference in the mean energy to break between the wool yarns exposed to wet (n=210) conditions and those which were dry (n=210). The decrease in tensile strength of the wet wool counteracted the increase in extension at break of these yarns resulting in no net change in energy to break.

In summary, the energy at break for the wool yarns exposed to 60 days of continuous freezing was found to be significantly higher than the energy at break of the wool yarns exposed to continuous freezing for 0, 20, and 40 days. This increase in energy at break relates to the significant increase in extension at break experienced by the wool yarns exposed to 60 days of continuous freezing. Although, the wool yarns exposed to 20 cycles of freezing and thawing also experienced a significant increase in extension at break, this increase was not as severe as that of the wool yarns exposed to 60 days of continuous freezing, explaining the lack of significance in the change in energy at break for these wool yarns.

Summary of Tensile Testing Results

The following three null hypotheses concerning the tensile properties of the wool yarns were tested:

Null Hypothesis 1. There is no significant difference in the tensile strength of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Null Hypothesis 2. There is no significant difference in the extension at break of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Null Hypothesis 3. There is no significant difference in the energy to break the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Statistical analyses indicated that there were no significant effects due to the interaction of the conditioning and freezing treatments on the tensile strength, extension at break, and energy to break the wool yarns after 60 days of freezing exposure. There were significant effects due to each of the independent variables, the conditioning treatment (dry or wet) and the freezing treatment (cyclical or continuous); on this basis the null hypotheses could be rejected. However, on the basis that there were no effects due to the interaction of each of the conditioning and freezing treatments for 60 days the null hypotheses can be **accepted**.

Effects Due to Conditioning Treatment

The wool yarns which had been wet prior to testing were 2% weaker and 2% more extensible than the yarns which were exposed to dry conditions. This was a result of the dry or wet condition alone, rather than due to a combination of effects due to the condition of the wool and the freezing treatment. Although the wet yarns decreased in strength, they increased in elongation; therefore, there was no significant difference in the area under the stress-strain curve, or energy at break. Wool fibres may swell when exposed to moisture, resulting in a general weakening of fibres tested while in a wet condition (Windle, 1956). Although the fibres were dried and reconditioned prior to testing, it is possible that there may have been some permanent rearrangement of molecules in the fibres which were exposed to wet conditions. Molecular rearrangement, such as an increase in the size of the intermolecular spaces, resulting

from the swelling due to moisture, leads to an increase in extension and decrease in tensile strength of wool (Watt, 1980; Windle).

Effects Due to Freezing Treatment

There was a significant effect due to the freezing treatment on the extension at break and energy to break the wool yarns, regardless of whether the yarns were in a dry or wet condition during freezing. After 60 days of continuous freezing, there was a significant increase in extension at break and in energy to break the wool yarns. Increases in both tensile strength and extension at break can affect the energy at break by increasing the area under the stress-strain curve (Morton & Hearle, 1975, p. 269). The increase in energy to break the wool yarns after 60 days of continuous freezing was a result of the significant increase in extension at break exhibited by these yarns.

Extensibility may increase when molecules in amorphous areas have increased ability to slide past one another (Merkel, 1991). The increase in extension at break after 60 days of continuous freezing suggests changes in the amorphous regions of the wool fibres, resulting in increased ease of molecular slippage under tension and increased extension at break. Although the spaces in the wool fibres are not large enough to accommodate ice crystals which might physically break molecular bonds, it is possible that, after 60 days of freezing, the moisture present in the wool fibres could cause sufficient swelling to rearrange molecules or alter intermolecular bonds resulting in an increase in breaking extension.

Cyclical freezing vs. continuous freezing. Whether yarns were cyclically frozen or continuously frozen for up to 60 days, there were no differences between the two types of freezing in the wool yarn tensile properties. Comparisons of tensile strength, extension at break, and energy at break for the wool yarns that had been exposed to the same length of freezing (eg. 0, 20, 40, or 60 days), but different types of freezing (freeze-thaw vs. continuous) suggest no statistically significant differences.

Effect of length of freezing treatment. There were no significant differences in tensile strength or in energy to break among the wool yarns exposed to freezing and thawing; however, the wool yarns exposed to 20 cycles of freezing and thawing were found to have a significantly higher extension at break than the unfrozen yarns and the yarns exposed to 40 cycles of freezing and thawing. The extension at break for these wool yarns is consistently higher than that of the yarns exposed to other freezing treatments, and the tensile strength and energy at break for this sample are not significantly different than those of any of the other yarns. It is unlikely that the 20 cycles of freezing and thawing caused any changes in the intermolecular bonding in the fibres and the differences may be due to experimental error in testing or are a result of natural variability in the yarns.

Among the yarns exposed to continuous freezing, the yarns frozen continuously for 60 days exhibit the most differences. They were found to have a significantly higher mean extension at break than the unfrozen yarns and the yarns exposed to 20 and 40 days of continuous freezing. This same relationship occurs with the energy at break of these sets of wool yarns.

In summary, the highest extension at break, and energy at break occur with the yarns frozen continuously for 60 days. The increase in energy at break directly relates to the increase in extension at break. The increase in extension at break suggests changes in the amorphous regions of the wool fibres, resulting in increased ease of molecular slippage under tension and increased extension at break, occurring at some point between 40 and 60 days of continuous freezing.

Moisture Sorption Isotherms and Moisture Regain

The moisture sorption behavior of wool may change if there is a change in the intermolecular bonds within the fibres as a result of the conditioning and freezing treatments. A decrease in moisture regain means that less water is being sorbed by the fibres. This would suggest fewer binding sites within the fibre molecular structure or less intermolecular space for

aggregation of water molecules, indicating possible collapse of the fibre structure. Increases in regain would suggest more binding sites for water molecules and/or increases in the size or number of intermolecular spaces. In such a case, broken bonds and physical separation of the molecules within the fibres are possible. The literature suggests that the intermolecular spaces are too small to accommodate ice crystals which could physically damage the molecular structure of the wool fibres (Alexander et al., 1963; Hoeve, 1980; Rothmayr, 1975). Swelling in the fibre due to the sorbed moisture, however, might physically break intermolecular bonds such as salt links or H-bonds (Breuer, Buras, & Fookson, 1980; Hoeve, 1980).

The moisture regain at 6 levels of relative humidity (11%, 32%, 53%, 65%, 75%, and 97%) was determined for wool yarns exposed to dry or wet conditions while cyclically or continuously frozen for 0, 20, 40, or 60 days. The moisture regain at each relative humidity was calculated using Equation 10, (%R = 100 (M2-M1)/M1). Raw data for the moisture regain determinations are presented in Appendix A-3.

The moisture regain values obtained after exposure to the atmosphere above saturated salt solutions were expected to be reasonable estimates of the moisture regain of the wool at each relative humidity. Although this method does not have the highest accuracy when compared to other commonly used methods (Labuza, 1984; Troller & Christian, 1978), it was chosen because of its ease of use and the availability and low cost of the equipment and chemicals required. The moisture regain values at 11%, 32%, and 97% were difficult to determine due to rapid changes in moisture content of the yarns upon removal from the humidity chambers for weighing. Although moisture regain values at these relative humidities are reported, the discussion will primarily be concerned with the more reliable moisture regain values at 53%, 65%, and 75% RH.

Moisture Sorption Isotherms

An isotherm of the average regain of three wool specimens at each relative humidity was plotted for each set of wool yarns exposed to the various freezing treatments. The yarns

were equilibrated directly to the desired relative humidity from the dry state; the isotherms produced are adsorption isotherms. The 14 resulting isotherms are presented in Appendix A-4. Differences among the isotherms are not easily determined by visual evaluation of the plots.

Even though the isotherms for the wool yarns exposed to continuous freezing for 60 days appear to be the most different from the isotherm for the unfrozen dry wool, it can be seen in Figure 11 that the difference between these isotherms is minimal. Comparisons of the moisture regain values at each relative humidity between the unfrozen dry wool, the wool frozen continuously for 60 days while dry and that frozen continuously for 60 days while wet reveal few significant differences. There is one point at which the isotherms for the yarns exposed to these three treatments significantly differ. At 32% RH the moisture regain of the yarns continuously frozen while wet was 8.16%. This was significantly higher than the moisture of the unfrozen dry wool (7.67%), and the dry wool continuously frozen (7.72%). In spite of the difference noted, these three experimental isotherms are in general agreement with the isotherm plotted from the data of Speakman and Cooper (1936) (Figure 12).

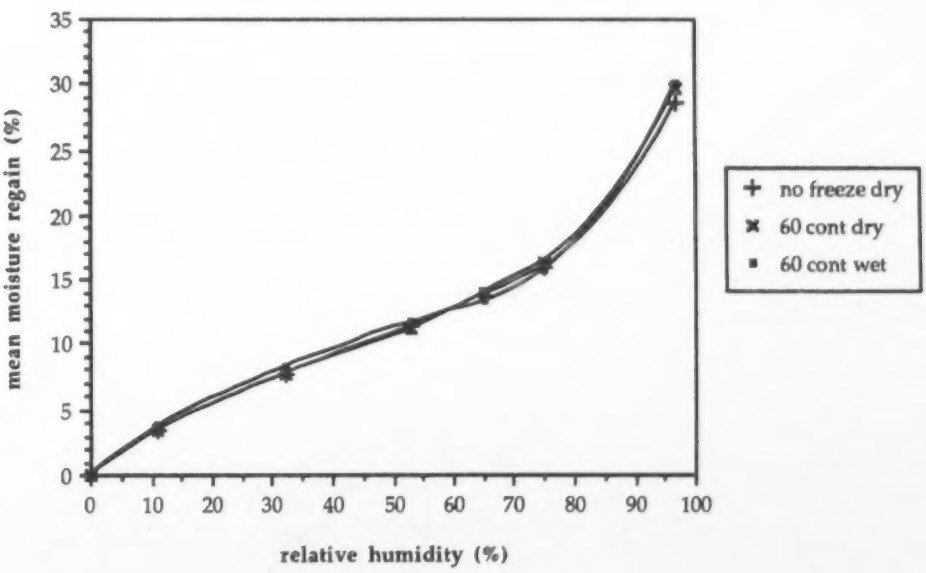

Figure 11: Moisture sorption isotherms for unfrozen dry wool yarns, wool yarns frozen while dry and those frozen while wet for 60 days.

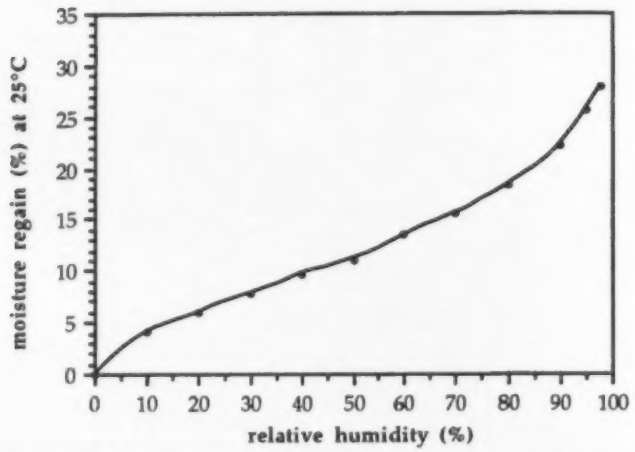

Figure 12: Moisture sorption isotherm for wool at 25°C from the data of Speakman and Cooper (1936).

Moisture Regain at 11%, 32%, 53%, 65%, 75% and 97% RH

Figures 13-18 illustrate the moisture regain (%) at 11%, 32%, 53%, 65%, 75%, and 97% RH of wool yarns after 0, 20, 40, and 60 days of cyclical or continuous freezing while in a dry or wet condition. The range of regain values at each relative humidity is relatively small; for example, at 65% RH, the standard relative humidity for measuring moisture regain, the regain values range from 13.18% to 13.97%. These values are in good agreement with the standard Canadian commercial moisture regain value of 13.6% for wool (CAN/CGSB-4.2 No. 0-M88).

A two-way analysis of variance was performed on the dependent variables of moisture regain at 11%, 32%, 53%, 65%, 75%, and 97% RH vs. the independent variables of conditioning treatment (dry or wet) and freezing treatment (cyclical or continuous freezing for 0, 20, 40, or 60 days). There were significant interaction effects (α=0.05) of the two independent variables at each relative humidity except at 97% RH where there was a significant effect due to the freezing treatment only. In order to determine which freezing conditions caused significant changes in the wool fibres, multiple comparisons of the treatment means for each relative humidity were carried out using Scheffé's test (α=0.05). The moisture regain results and statistical analyses are summarized in Tables 8-13.

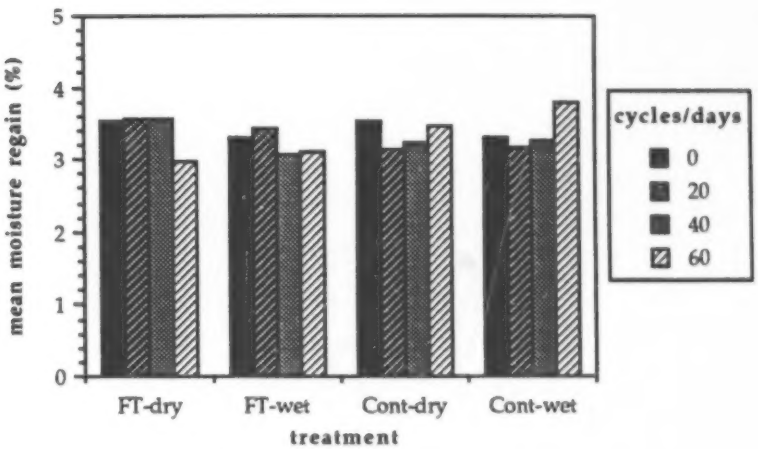

Figure 13: Moisture regain at 11% RH of wool yarns exposed to dry or wet conditions and freezing treatments.

Table 8
Moisture Regain at 11% Relative Humidity of Wool Yarns Exposed to Continuous Freezing or Multiple Freeze-Thaw Cycles While in a Dry or Wet Condition

Freezing Treatment	Dry		Wet	
	Mean Regain (%)	% change[a]	Mean Regain (%)	% change[a]
No Freezing	$3.54_{a,b}$		$3.30_{b,c,d,e}$	-6.8
Freeze-Thaw (cycles)				
20	$3.57_{a,b}$	+0.8	$3.42_{b,c,d}$	+3.4
40	$3.56_{a,b}$	+0.6	3.08_{e}	-13.0*
60	2.96_{e}	-16.4*	$3.12_{d,e}$	-11.9*
Continuous Freeze (days)				
20	$3.14_{c,d,e}$	-11.3*	$3.18_{c,d,e}$	-10.2*
40	$3.23_{b,c,d,e}$	-8.8	$3.26_{b,c,d,e}$	-7.9
60	$3.47_{a,b,c}$	-2.0	3.78_{a}	+6.8

Note 1. Mean of n=3 yarns from each treatment.
Note 2. Means indicated with the same subscript are not significantly different at α=0.05 as determined by Scheffé's test.
[a] % change when compared to the dry unfrozen control.
* statistically significant change

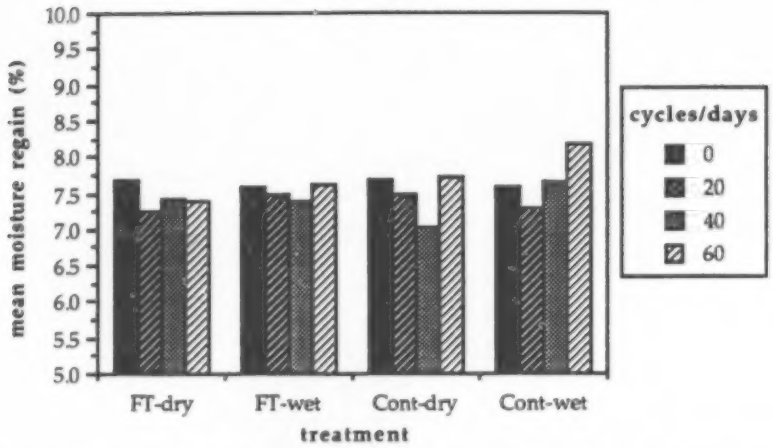

Figure 14: Moisture regain at 32% RH of wool yarns exposed to dry or wet conditions and freezing treatments.

Table 9
Moisture Regain at 32% Relative Humidity of Wool Yarns Exposed to Continuous Freezing or Multiple Freeze-Thaw Cycles While in a Dry or Wet Condition

Freezing Treatment	Dry		Wet	
	Mean Regain (%)	% change[a]	Mean Regain (%)	% change[a]
No Freezing	$7.67_{a,b}$		$7.58_{a,b,c}$	-1.2
Freeze-Thaw (cycles)				
20	$7.25_{d,e}$	-5.5*	$7.49_{a,b,c,d}$	-2.3
40	$7.42_{b,c,d}$	-3.3	$7.39_{c,d}$	-3.7*
60	$7.39_{c,d}$	-3.7*	$7.62_{a,b,c}$	-0.7
Continuous Freeze (days)				
20	$7.47_{a,b,c,d}$	-2.6	7.29_{d}	-5.0*
40	7.01_{e}	-8.6*	$7.65_{a,b,c}$	-0.3
60	7.72_{a}	+0.7	8.16_{f}	+6.4*

Note 1. Mean of n=3 yarns from each treatment.
Note 2. Means indicated with the same subscript are not significantly different at α=0.05 as determined by Scheffé's Test.
[a] % change when compared to the dry unfrozen control
* statistically significant change

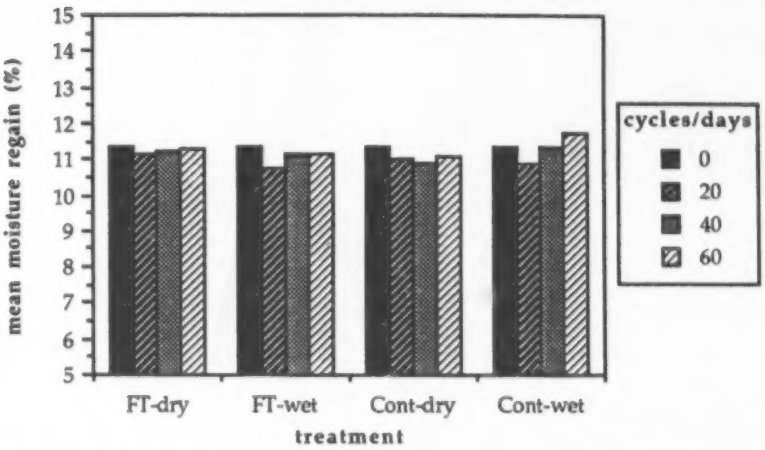

Figure 15: Moisture regain at 53% RH of wool yarns exposed to dry or wet conditions and freezing treatments.

Table 10
Moisture Regain at 53% Relative Humidity of Wool Yarns Exposed to Continuous Freezing or Multiple Freeze-Thaw Cycles While in a Dry or Wet Condition

Freezing Treatment	Dry		Wet	
	Mean Regain (%)	% change[a]	Mean Regain (%)	% change[a]
No Freezing	$11.36_{a,b}$		$11.31_{a,b,c}$	-0.4
Freeze-Thaw (cycles)				
20	$11.16_{b,c}$	-1.8	10.76_{c}	-5.3*
40	$11.18_{b,c}$	-1.6	$11.14_{b,c}$	-2.0
60	$11.25_{a,b,c}$	-1.0	$11.14_{b,c}$	-2.0
Continuous Freeze (days)				
20	$11.03_{b,c}$	-2.9	$10.90_{b,c}$	-4.0
40	$10.90_{b,c}$	-4.0	$11.33_{a,b}$	-0.3
60	$11.05_{b,c}$	-2.7	11.75_{a}	+3.4

Note 1. Mean of n=3 yarns from each treatment.
Note 2. Means indicated with the same subscript are not significantly different at α=0.05 as determined by Scheffé's test.
[a] % change when compared to the dry unfrozen control
* statistically significant change

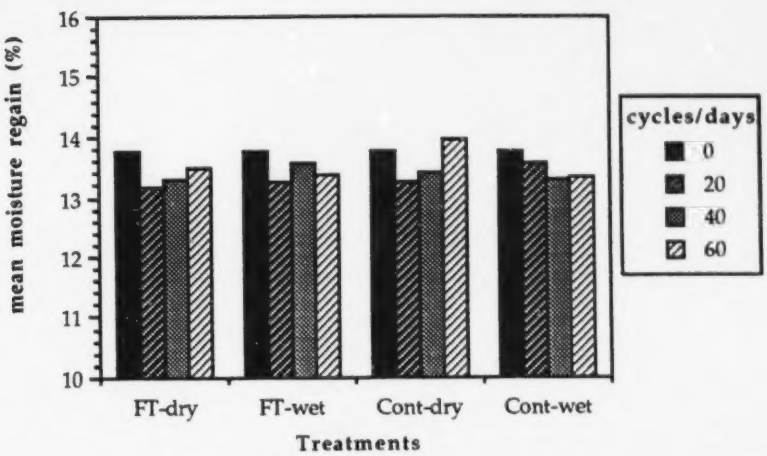

Figure 16: Moisture regain at 65% RH of wool yarns exposed to dry or wet conditions and freezing treatments.

Table 11
Moisture Regain at 65% Relative Humidity of Wool Yarns Exposed to Continuous Freezing or Multiple Freeze-Thaw Cycles While in a Dry or Wet Condition

Freezing Treatment	Dry		Wet	
	Mean Regain (%)	% change[a]	Mean Regain (%)	% change[a]
No Freezing	$13.78_{a,b}$		$13.76_{a,b,c}$	-0.1
Freeze-Thaw (cycles)				
20	13.18_{d}	-4.4*	13.25_{d}	-3.8*
40	$13.30_{b,c,d}$	-3.5	$13.47_{a,b,c,d}$	-2.2
60	$13.48_{a,b,c,d}$	-2.2	$13.38_{b,c,d}$	-2.9
Continuous Freeze (days)				
20	$13.26_{c,d}$	-3.8*	$13.57_{a,b,c,d}$	-1.5
40	$13.43_{b,c,d}$	-2.5	$13.28_{b,c,d}$	-3.6
60	13.97_{a}	+1.4	$13.32_{b,c,d}$	-3.3

Note 1. Mean of n=3 yarns from each treatment.
Note 2. Means indicated with the same subscript are not significantly different at α=0.05 as determined by Scheffé's test.
[a] % change when compared to the dry unfrozen control.
* statistically significant change

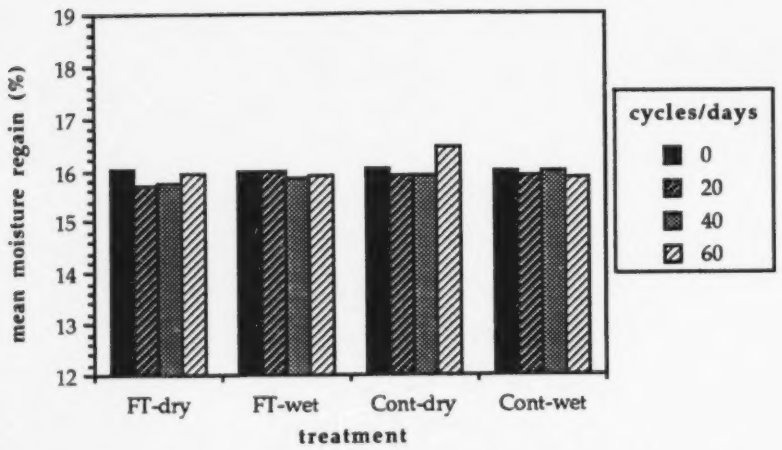

Figure 17: Moisture regain at 75% RH of wool yarns exposed to dry or wet conditions and freezing treatments.

Table 12
Moisture Regain at 75% Relative Humidity of Wool Yarns Exposed to Continuous Freezing or Multiple Freeze-Thaw Cycles While in a Dry or Wet Condition

Freezing Treatment	Dry		Wet	
	Mean Regain (%)	% change[a]	Mean Regain (%)	% change[a]
No Freezing	$16.03_{a,b}$		$16.00_{a,b}$	-0.2
Freeze-Thaw (cycles)				
20	15.71_{b}	-2.2	$16.00_{a,b}$	-0.2
40	15.75_{b}	-1.7	15.83_{b}	-1.2
60	15.92_{b}	-0.7	15.90_{b}	-0.8
Continuous Freeze (days)				
20	15.91_{b}	-0.7	15.89_{b}	-0.9
40	15.90_{b}	-0.8	$15.97_{a,b}$	-0.4
60	16.42_{a}	+2.4	15.83_{b}	-1.2

Note 1. Mean of n=3 yarns from each treatment.
Note 2. Means indicated with the same subscript are not significantly different at α=0.05 as determined by Scheffé's test.
[a] % change when compared to the dry unfrozen control.
* statistically significant change

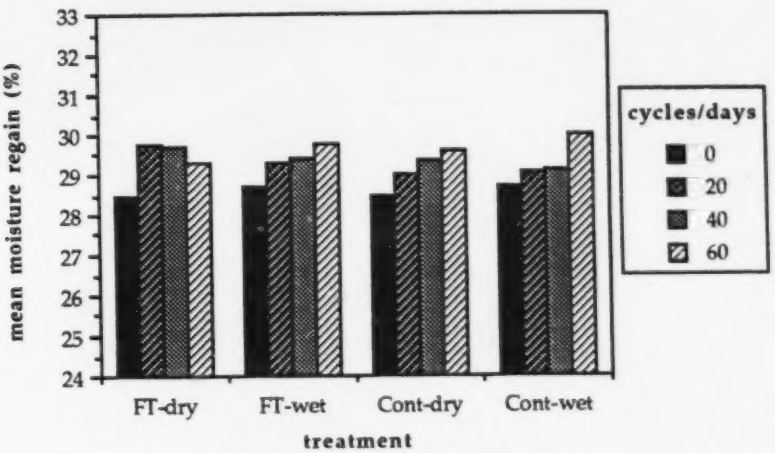

Figure 18: Moisture regain at 97% RH of wool yarns exposed to dry or wet conditions and freezing treatments.

Table 13
Moisture Regain at 97% Relative Humidity of Wool Yarns Exposed to Continuous Freezing or Multiple Freeze-Thaw Cycles While in a Dry or Wet Condition

Freezing Treatment	Mean Regain (%)	% change[a]
No Freezing	28.60_{a}	
Freeze-Thaw (cycles)		
20	$29.53_{a,b}$	+3.3
40	$29.56_{a,b}$	+3.4
60	$29.55_{a,b}$	+3.3
Continuous Freeze (days)		
20	$29.02_{a,b}$	+1.5
40	$29.22_{a,b}$	+2.2
60	29.80_{b}	+4.2*

Note 1. Mean of n=6 yarns from each treatment.
Note 2. Means indicated with the same subscript are not significantly different at α=0.05 as determined by Scheffé's test.
[a] % change when compared to the dry unfrozen control.
* statistically significant change

At each relative humidity there were no statistical differences in the moisture regain between the dry unfrozen wool and the wet unfrozen wool (which had been wet out, dried, and reconditioned prior to testing). Exposure to wet conditions prior to testing, therefore, did not significantly affect the moisture regain of the wool. When changes in the moisture regain at each relative humidity were determined, the regain of the dry unfrozen yarns was used as the control and represented the original condition of the wool. Of primary concern are changes in the moisture sorption of the wool after 60 days of freezing, the longest exposure period.

Effect of Condition and Freezing Treatment on Moisture Regain After 60 Days

The following six null hypotheses concerning changes in the moisture regain of the wool yarns after 60 days of exposure to freezing were tested:

Null Hypothesis 4. There is no significant difference in the moisture regain at 11% RH of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Reject: There were significant decreases in moisture regain at 11% RH for the wool yarns cyclically frozen while dry and those cyclically frozen while wet for 60 days.

Null Hypothesis 5. There is no significant difference in the moisture regain at 32% RH of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Reject: There were significant decreases in moisture regain at 32% RH for the wool yarns cyclically frozen while dry and those continuously frozen while wet for 60 days.

Null Hypothesis 6. There is no significant difference in the moisture regain at 53% RH of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Accept: After 60 days of freezing there were no significant changes in the moisture regain at 53% RH of the wool yarns exposed to cyclical freezing and thawing or to continuous freezing regardless of whether they were in a wet or dry condition.

Null Hypothesis 7. There is no significant difference in the moisture regain at 65% RH of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Accept: After 60 days of freezing there were no significant changes in the moisture regain at 65% of the wool yarns exposed to cyclical freezing and thawing or to continuous freezing regardless of whether they were in a wet or dry condition.

Null Hypothesis 8. There is no significant difference in the moisture regain at 75% RH of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Accept: After 60 days of freezing there were no significant changes in the moisture regain at 75% RH of the wool yarns exposed to cyclical freezing and thawing or to continuous freezing regardless of whether they were in a wet or dry condition.

Null Hypothesis 9. There is no significant difference in the moisture regain at 97% RH of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Accept: On the basis that there was no significant effect due to the interaction of the conditioning and freezing treatments on the moisture regain of the wool yarns at 97% RH. After 60 days of continuous freezing, however, regardless of whether the wool was in a dry or wet condition, there was a significant increase in the moisture regain at 97% RH. This increase is a result of the freezing treatment alone with no effect due to the dry or wet condition of the wool.

After 60 days of freezing, there were no significant changes in moisture regain at 53%, 65%, and 75% RH. These results suggest that there were no changes in the intermolecular bonds or spaces within the wool fibre after exposure to 60 days of freezing treatment. The weighings were most reliable at these relative humidities and these results should be given the most consideration; it is interesting, however, to note the results at the other relative humidities.

At the lowest and highest relative humidities (11% and 97% RH) there were some significant changes, but these included both increases and decreases in moisture regain. At 11% RH, for example, both the dry and wet cyclically frozen wool yarns, showed significant decreases in moisture regain by 16.4% and 11.9% respectively (Table 8). At 97% RH, there was a significant 4.2% increase in the moisture regain of the wool yarns continuously frozen for 60 days, regardless of whether they were in a dry or wet state (Table 13). At 32% RH (Table 9) there was a 3.7% decrease in moisture regain in the dry wool yarns exposed to 60 freeze-thaw cycles and a 6.4% increase in moisture regain in the wet wool yarns exposed to continuous freezing for 60 days. At both 11% and 32% RH, the moisture regain of the dry cyclically frozen yarns decreased suggesting that wool which has been cyclically frozen while dry for 60 days has fewer binding sites for water molecules than the unfrozen wool. The decreases in moisture

regain identified at 11% and 32% RH are not consistent with the results at the other relative humidities tested.

Although there were increases in moisture regain at 32% and 97% RH after 60 days for the continuously frozen yarns, these increases can not be compared. At 97% there was no effect due to the dry or wet condition of the wool; therefore, it **cannot** be said that the *wet* yarns exposed to 60 days of continuous freezing changed significantly, only that the 60 day continuous freezing treatment caused a significant increase. The increase in moisture regain at 97% RH for the wool yarns continuously frozen for 60 days may indicate a possible increase in intermolecular spaces or amorphous regions where water molecules may accumulate in the fibres at this high relative humidity. The presence of larger intermolecular spaces could also explain the extension at break results for the same 60 days of continuous freezing sample.

The previously discussed changes in moisture regain were based on comparisons made between the unfrozen dry wool and the wool yarns exposed to each of the various freezing treatments. In addition to these changes in moisture regain, there are significant differences in moisture regain at 11%, 32%, 53%, 65%, 75%, and 97% RH between the wool yarns exposed to the various freezing treatments. Three types of comparisons between significantly different treatment means are noted: 1. wool frozen dry vs. wool frozen wet, with freezing type (cyclical or continuous) and length of freezing constant; 2. wool frozen cyclically vs. wool frozen continuously, with condition (dry or wet) and length of freezing constant; and 3. wool frozen for different periods of time, with freezing type and condition constant.

Wool Frozen Dry vs. Wool Frozen Wet

Differences in moisture regain between the wool frozen while dry and the wool frozen while wet after 60 days occur only with the yarns which have been continuously frozen. At 32% and 53% RH the moisture regain values of the wool yarn frozen continuously for 60 days while dry were significantly lower than the regain of the wet wool yarns exposed to 60 days of continuous freezing (Tables 9 & 10). On the other hand, at 65% and 75% RH, the moisture

regain values of the wool yarns frozen continuously for 60 days while dry were significantly higher than those of the wool frozen for 60 days while wet (Tables 11 & 12). The apparent contradiction of these results makes it difficult to draw conclusions regarding the influence of the dry or wet condition of the wool during freezing on the moisture sorption properties of the wool yarns.

Cyclical Freezing vs. Continuous Freezing

After 60 days of freezing, it was found that the moisture regain values of the *continuously* frozen *dry* wool yarns were significantly *higher* than that of the *cyclically* frozen *dry* wool yarns at 11%, 32%, and 75% RH (Tables 8, 9, 12). The moisture regain of *continuously* frozen *wet* wool was significantly *higher* than the *cyclically* frozen *wet* wool at 11%, 32%, and 53% RH (Tables 8, 9, 10). When wool was exposed to freezing for periods up to 40 days, there were no significant differences in the moisture regain at 53%, 65%, and 75% RH between the wool frozen cyclically and the wool frozen continuously, while in the same dry or wet condition. These results suggest that after exposures to the freezing treatments longer than 40 days, the continuous freezing treatment has a significantly different effect than the cyclical freezing treatment on the moisture regain behavior of the wool yarns. Even at freezing temperatures, some water molecules within the wool fibre are mobile (Lynch & Webster, 1979). Prolonged exposure to continuous freezing may allow water molecules to move within the fibre and possibly collect in areas which are prone to swelling, eg. matrix and intercellular cement (Breuer et al., 1980). Increased water content in these regions may result in the breaking of intermolecular bonds (eg. H-bonds or salt links) within the fibre as a result of swelling. These broken bonds may provide new binding sites for water molecules in the fibres after the yarns have thawed and dried.

Effect of Length of Freezing Treatment

Although the changes in moisture regain after 60 days were of primary concern, there were some changes after shorter exposures to conditioning and freezing treatments as well as

differences in moisture regain between wool yarns which had been exposed to the same treatments but different periods of exposure. In many cases these changes or differences were not consistent throughout each group of yarns exposed to the same freezing and conditioning types but for different periods.

There were no significant differences in moisture regain at 53%, 65% and 75% RH among the wool yarns cyclically frozen while in either a dry or a wet condition. Among the wool yarns which were dry during continuous freezing the moisture regain values at 65% and 75% RH of the yarns frozen for 60 days were significantly higher than the moisture regain values of those frozen for 20 days and for 40 days. Among the wool yarns exposed to continuous freezing while wet, the moisture regain at 53% RH of the yarns frozen for 60 days was significantly higher than the regain of the yarns frozen for 20 days.

There was frequently a significant decrease in moisture regain after 20 cycles or days of exposure to cyclical or continuous freezing when compared to the unfrozen dry wool yarns. The wool yarns frozen *cyclically while dry* showed significant decreases in moisture regain at 32% and 65% RH (Tables 9 and 11). After 20 days of freezing, the wool yarns frozen *cyclically while wet* showed a significant decrease in moisture regain at 53% and 65% RH (Tables 10 and 11). The wool yarns frozen *continuously while dry* for 20 days exhibited significant decreases in moisture regain at 11% and 65% RH (Tables 8 and 11). The wool yarns exposed to 20 days of *continuous freezing while wet* exhibited significant decreases in moisture regain at 11% and 32% RH (Tables 8 and 9); however, after 60 days, the moisture regain at 32% RH of the continuously frozen wet yarns significantly increased. Overall, these moisture regain results determined after 20 days of exposure to freezing treatment are unusual. It is possible that there are some initial changes in the fibres which may be reversed as exposure period increases. The differences may also be the result of experimental error.

In summary, across the range of relative humidities studied, there is not one set of wool yarns exposed to the same conditioning and freezing treatments which has consistently

different moisture regain values. The yarns frozen continuously for 60 days, whether in a dry or wet condition, tend to have higher moisture regain and occur most frequently in significantly different pairs. Although the observations suggest that after 60 days of continuous freezing, moisture regain tends to increase, it must be remembered that the range of regain values is relatively small at each RH tested. Also, the method used for determination of moisture regain does not have the highest accuracy compared to other methods (Labuza, 1984; Troller & Christian, 1978) and at the relative humidities which were considered to be the most reliable, eg. 53%, 65%, and 75% RH, there were no significant changes after 60 days.

BET Monolayer Value

The BET monolayer value is used to estimate the amount of bound water in a fibre. It represents the moisture regain (%) at which a single layer of water molecules, or monomolecular layer of water, is formed on the available water binding sites in the fibre (eg. polar side chains) (Morton & Hearle, 1975). BET plots were made using the moisture regain values at 11%, 32%, and 53% RH for each of the wool yarns exposed to cyclical or continuous freezing for 0, 20, 40, or 60 days while in a wet or dry condition. An example of a BET plot and calculations of monolayer value using Equation 7 can be found in Appendix A-1. The individual BET values calculated are provided in Appendix A-3.

Figure 19 illustrates the mean BET monolayer values of wool yarns after 0, 20, 40, and 60 days of cyclical or continuous freezing while in a dry or wet state. The BET monolayer values of the frozen wool yarns range from 5.58% to 6.13% regain. These values are close to the value of 6.58% for wool reported in Morton and Hearle (1975, p. 245). The BET monolayer values of the frozen yarns, in general, show no consistent increase or decrease when compared to the unfrozen yarns. The change in mean BET monolayer value ranged from a 5.4% decrease to a 4% increase as shown in Table 14. These changes from the original were not found to be significant, thus the exposure of wool yarns to freezing conditions for up to 60 days did not affect the formation of a monolayer of water molecules within the wool fibres.

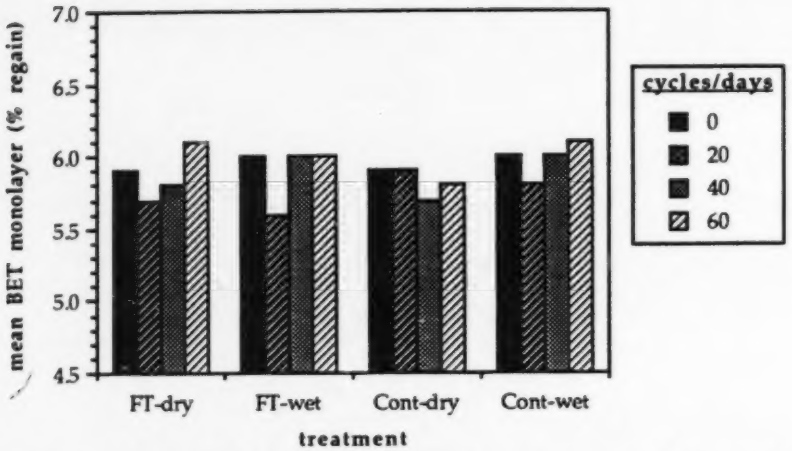

Figure 19: BET monolayer value of wool yarns exposed to wet or dry conditions and freezing treatments.

Table 14
BET Monolayer Values of Wool Yarns Exposed to Continuous Freezing or Multiple Freeze-Thaw Cycles While in a Dry or Wet Condition

	Dry		Wet	
Freezing Treatment	BET Monolayer (% regain)	% change[a]	BET Monolayer (% regain)	% change[a]
No Freezing	$5.90_{a,b,c,d}$		$5.99_{a,b,c}$	+1.5
Freeze-Thaw (cycles)				
20	$5.74_{b,c,d}$	-2.7	5.58_{d}	-5.4
40	$5.76_{b,c,d}$	-2.4	$5.98_{a,b,c}$	+1.4
60	6.13_{a}	+4.0	$5.98_{a,b,c}$	+1.4
Continuous Freeze (days)				
20	$5.88_{a,b,c,d}$	-0.3	$5.76_{b,c,d}$	-2.4
40	$5.71_{c,d}$	-3.2	$6.02_{a,b,c}$	+2.0
60	$5.76_{b,c,d}$	-2.4	$6.08_{a,b}$	+3.1

Note 1. Mean of n=3 yarns from each freezing treatment.
Note 2. Means indicated with the same subscript are not significantly different at α=0.05 as determined by Scheffé's test.
[a] % change when compared to the dry unfrozen control.
* statistically significant change

The individual BET monolayer values were statistically analyzed by a two-way analysis of variance with multiple comparisons using Scheffé's test (α=0.05). Table 14 summarizes the BET monolayer values calculated and statistical analyses for the wool yarns exposed to the various freezing treatments. There were no statistical differences in the mean BET monolayer value between the dry unfrozen wool and the wet unfrozen wool (which had been wet out, dried, and reconditioned prior to testing). Exposure to wet conditions prior to testing, therefore, did not significantly change the moisture content at which a BET monolayer forms. When changes in the monolayer value were determined, the dry unfrozen yarns were used as the control and represented the original condition of the wool.

Changes in the BET Monolayer Value After 60 Days

The following null hypothesis concerning the changes in the BET monolayer value of the wool yarns after exposure to conditioning and freezing treatments for 60 days was tested:

Null Hypothesis 10. There is no significant difference in the BET monolayer value of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Accept: After 60 days of exposure to dry or wet conditions and cyclical or continuous freezing, there was no significant change in the BET monolayer values of the wool yarns.

Significant differences in BET monolayer value among the wool yarns exposed to the 14 conditioning and freezing treatment combinations (eg. other than comparisons involving the control) are identified in Table 14. Three types of comparisons between significantly different treatment means are discussed: 1. wool frozen dry vs. wool frozen wet, with freezing type and length of freezing constant; 2. wool frozen cyclically vs. wool frozen continuously, with length of freezing and condition (eg. dry or wet) constant; and 3. wool frozen for different periods, with freezing and conditioning treatments constant.

Wool Frozen Dry vs. Wool Frozen Wet

There were no differences in the BET monolayer values of the wool yarns frozen wet

compared to the wool yarns frozen dry when they were frozen by the same type of freezing (cyclical or continuous) for the same period (0, 20, 40, or 60 days).

Cyclical Freezing vs. Continuous Freezing.

After 60 days, the dry wool yarns which were frozen and thawed had a higher BET monolayer value (6.13%) than the dry wool yarns which were continuously frozen for the same period (5.76%). The BET monolayer value of 6.13% for the dry wool yarns frozen and thawed 60 times was also higher than that for the dry wool yarns frozen and thawed 20 times (5.74%) and 40 times (5.76%). These results suggest that the monolayer value for the wool yarns exposed to 60 cycles of freezing and thawing while dry is unusually high. Higher monolayer values mean that a higher moisture regain is required to form a monolayer of water molecules on the available binding sites within the fibres, suggesting that *more* binding sites within the wool fibres are available. The monolayer results for the dry wool yarns cyclically frozen 60 times, however, are not consistent with the moisture regain results for this sample which were significantly low at 11% RH (2.90% regain) and 32% RH (7.39% regain). The low regain results of the dry wool after 60 freeze-thaw cycles suggest that there are *fewer* binding sites for water molecules.

Effect of Length of Freezing Treatment

There was an initial decrease in the BET monolayer values after 20 days. The moisture regain results identified several cases where there were initial decreases in regain after 20 days. The reduction in monolayer value is significant only in the case of the yarns cyclically frozen while wet for 20 days when compared to the *wet-treated unfrozen* yarns. The monolayer value of these wool yarns is the lowest value calculated. This significantly different BET monolayer value result for the wet 20 days of freezing and thawing sample is not consistent with the differences in moisture regain values for this sample, which were not significantly different from the wet unfrozen yarns at 11%, 32%, and 53% RH.

In summary, after 60 days of exposure to freezing treatments there are no significant increases or decreases in the BET monolayer values of the wool yarns. Freezing treatments, therefore, did not significantly alter the water binding sites within the wool fibres. A monomolecular layer of water forms in the wool fibres at approximately the same moisture regain in the wool yarns which had been exposed to freezing as in the unfrozen wool yarns.

Tributylphosphine-Alcoholic Sodium Iodide Solubility

Tributylphosphine-alcoholic sodium iodide (TASI) solubility was used to determine whether cleavage of the main chains in the wool protein had occurred as a result of cyclical or continuous freezing. The solubility value (%) reported is a measure of the soluble portion of the wool fibre extracted by treatment with the TASI reagent. An increase in solubility, shown as a decrease in residual mass, usually indicates a breakage of the peptide bonds of the molecular chain (Brown, 1972; Kilpatrick & Maclaren, 1970). A decrease in solubility, shown as an increase in residual mass, suggests that new intermolecular crosslinks, other than disulphide bonds, may have been introduced. These new crosslinks are usually ones which have been chemically introduced (Kilpatrick & Maclaren, 1970). The solubility values for the wool yarns exposed to each of the freezing treatments are presented in Appendix A-3.

Figure 20 illustrates the mean TASI solubility (%) of the wool yarns after 0, 20, 40, and 60 days of cyclical or continuous freezing while in a dry or wet condition. In spite of the variations of conditioning and freezing treatments, the solubility values shown in Table 15 are fairly consistent, ranging from 42.17% to 45.6% soluble matter. These values are lower than those of Kilpatrick and Maclaren (1970) who determined the solubility of two new merino wools after treatment with the TASI reagent to be 61% and 72%. Other reported TASI solubilities of new wool are 63% (Jones and White, 1971) and 59% (Kearns & Maclaren, 1979). Differences between the values reported for new wool in this study compared to those in the literature may be attributed to differences in the types of wool, or the specimen form (fibres, yarn, or fabric).

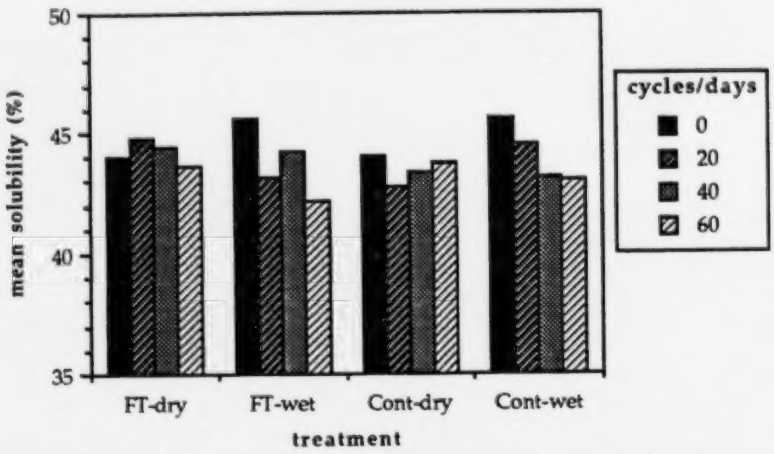

Figure 20: Tributylphosphine-alcoholic sodium iodide solubility of wool yarns exposed to dry or wet conditions and freezing treatments.

Table 15
Tributylphosphine-Alcoholic Sodium Iodide Solubility of Wool Yarns Exposed to Continuous Freezing or Multiple Freeze-Thaw Cycles While in a Dry or Wet Condition

	Dry		Wet	
Freezing Treatment	Solubility (%)	% change[a]	Solubility (%)	% change[a]
No Freezing	$43.99_{a,b,c}$		45.60_{a}	+3.7
Freeze-Thaw (cycles)				
20	$44.83_{a,b}$	+1.9	$43.05_{b,c}$	-2.1
40	$44.42_{a,b,c}$	+1.0	$44.19_{a,b,c}$	+0.5
60	$43.59_{a,b,c}$	-0.9	42.17_{c}	-4.1
Continuous Freeze (days)				
20	$42.74_{b,c}$	-2.8	$44.45_{a,b,c}$	+1.0
40	$43.28_{a,b,c}$	-1.6	$43.12_{a,b,c}$	-2.0
60	$43.67_{a,b,c}$	-0.7	$43.02_{b,c}$	-2.2

Note 1. Mean of n=2 yarns from each freezing treatment.
Note 2. Means indicated with the same subscript are significantly different at α=0.05 as determined by Scheffé's test.
[a] % change when compared to the dry unfrozen control.
* statistically significant change

A two-way analysis of variance performed on the dependent variable of mean TASI solubility of the wool vs. the independent variables of conditioning treatment (dry or wet) and freezing treatment (cyclical or continuous freezing for 0, 20, 40, or 60 days) indicated that there were significant interaction effects (α=0.05) of the two independent variables. Scheffé's multiple comparison procedure was used to compare the treatment means to determine which were significantly different at α=0.05. Table 15 summarizes the results of the solubility testing and statistical analyses for the wool yarns exposed to each of the conditioning and freezing treatments. Although the solubility of the wool yarns appeared to decrease after cyclical and continuous freezing, there were no statistically significant changes in solubility when the yarns exposed to freezing were compared to the dry unfrozen yarns The changes in TASI solubility for each set of yarns exposed to conditioning and freezing treatments when compared to the dry unfrozen wool ranged from a 4.1% decrease to a 3.7% increase.

Changes in the TASI Solubility After 60 Days

The following null hypothesis concerning the changes in the TASI solubility of the wool yarns after exposure to conditioning and freezing treatments for 60 days was tested:

Null Hypothesis 11. There is no significant difference in the tributylphosphine-alcoholic sodium iodide solubility of the wool yarns after exposure to each of the conditioning and freezing treatments for 60 days.

Accept: After 60 days of exposure to dry or wet conditions and cyclical or continuous freezing, there was no significant change in the tributylphosphine-alcoholic sodium iodide (TASI) solubility of the wool yarns. It was not believed that there would be physical damage to the peptide chains due to ice crystals. The results of TASI solubility testing suggest that there were no significant changes in the peptide chains of the wool fibres after exposure to conditioning and freezing treatments for 60 days when compared to the unfrozen dry control.

Three sets of wool yarns exposed to freezing while wet when compared to the *unfrozen wet-treated* wool exhibited significant differences. The mean TASI solubility of the wool

yarns cyclically frozen while wet 20 times (43.05%) and 60 times (42.17%), and the yarns continuously frozen while wet for 60 days (43.02%) were each significantly lower than the solubility of the wet unfrozen wool yarns (45.6%).

Statistically significant decreases in TASI solubility occur with the wet wool yarns which have been cyclically and continuously frozen only when they are compared to the unfrozen wet wool rather than the dry unfrozen yarns (control); therefore, it can not be concluded that the decreases are a result of the conditioning and freezing treatments. It is likely that the differences are due to natural variability in the yarns (eg. quantity of each fibre type present, thickness or yarn, *possible* presence of small pieces of grass or straw) as the differences involve the highest and lowest TASI solubility values reported.

Scanning Electron Microscopy (SEM)

SEM was used for qualitative evaluation of changes in the wool fibre appearance after freezing treatment. The microscopic appearance of fibres from the unfrozen dry wool yarns and from wool yarns exposed to the most severe freezing conditions, 60 days of cyclical or continuous freezing while in a dry or wet condition, were compared. Fibres of approximately the same size from each of the treatment groups showed no apparent differences in appearance. The appearance of the fibres in Plate 1 (720x magnification) is typical of the appearance of the fibres observed from yarns exposed to each of the freezing treatments. Plates 2-6 show typical fibres, of approximately the same diameter, from each of the treatment groups observed by SEM (1300x magnification). Note that none of these fibres exhibit surface cracking or fibrillation. Although they are not shown, fibre ends, where observed, remained intact.

Some of the coarser wool fibres showed vertical markings which looked like small ridges on the surface of the scales (Plates 7-8). These ridges appear close to the edges of the scales and also in regions where the scales have possibly been removed. Fibres exhibiting these markings were coarse and flat and were present in all samples examined, regardless of treatment. It is suspected that these markings may be related to the breed of the sheep or to

environmental conditions, such as light, which the wool fleece may have been exposed to during growth. As these markings were consistent in all samples observed, further investigation into the cause of these markings was not carried out.

After 60 days of cyclical or continuous freezing while in a wet or dry condition there were no apparent differences in fibre surface appearance. The results of Ito, Sakabe, Miyamoto, and Inagaki (1984) suggest that repeated cyclical freezing and thawing may cause fibrillation and surface cracking of wool fibres. In their investigation of textiles from the 1846 northern burial site of John Torrington of the Franklin Expedition, Kerr and Schweger (1989) noted fibrillation of wool fibres taken from the coffin lining and cover. Neither fibrillation nor surface cracking was observed in any of the fibres evaluated in this study. It is likely that other damaging factors, such as microorganisms, play a dominant role in causing the fibrillation of wool fibres in archaeological textiles.

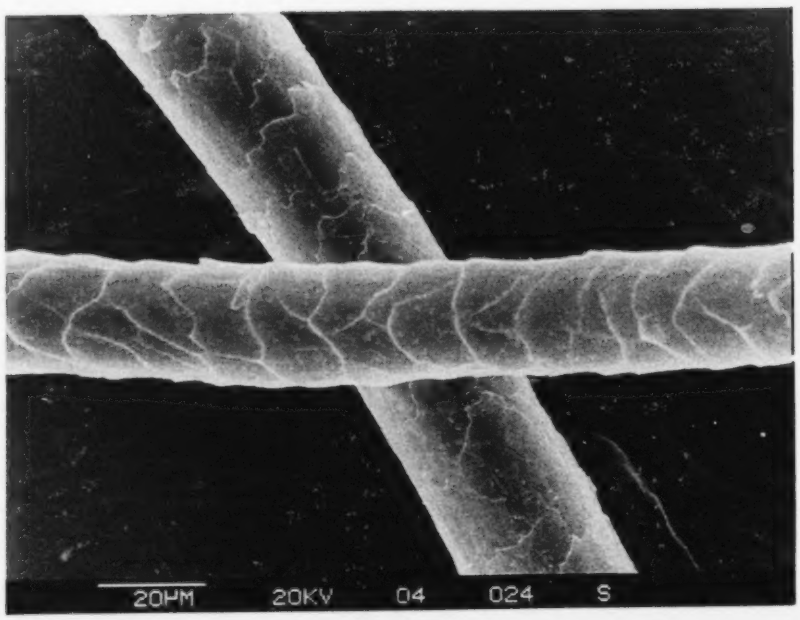

Plate 1. Wool fibres after 60 days of continuous freezing while dry (720x) are typical of all wool fibres examined.

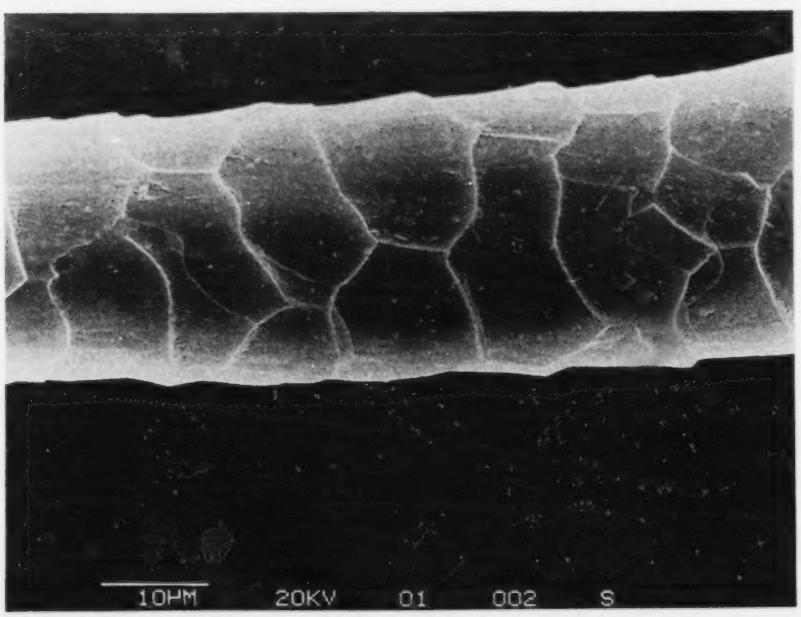

Plate 2. Wool fibre not subjected to freezing (1300x)

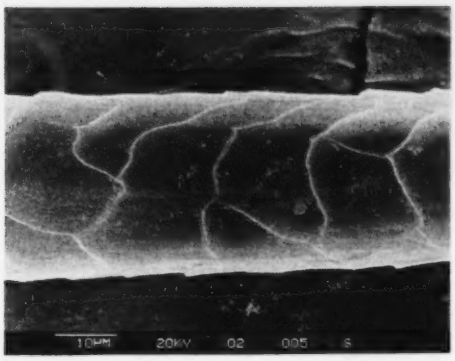

Plate 3. Wool fibre after 60 freezing-thawing cycles while dry (1300x).

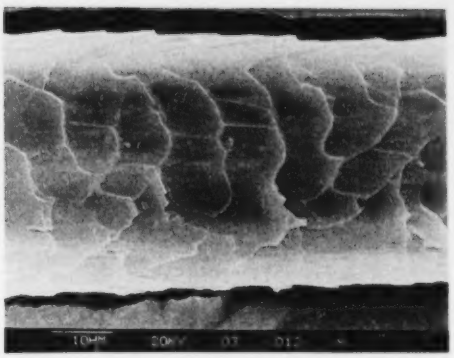

Plate 4. Wool fibre after 60 freezing-thawing cycles while wet (1300x)

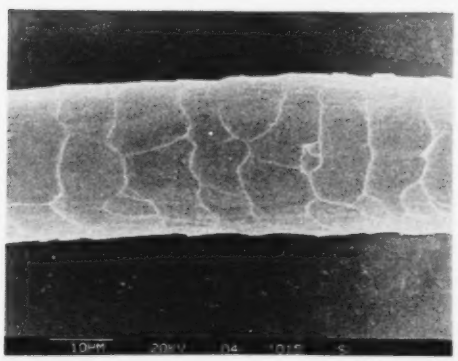

Plate 5. Wool fibre after 60 days of continuous freezing while dry (1300x)

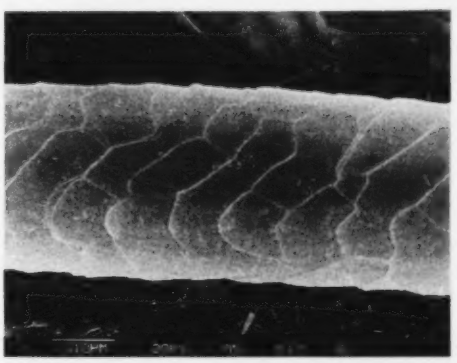

Plate 6. Wool fibre after 60 days of continuous freezing while wet (1300x)

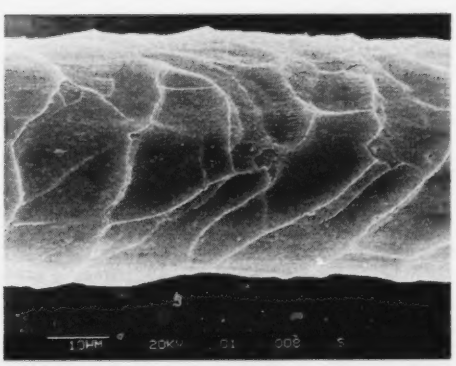

Plate 7. Typical example of the ridges observed on some coarse wool fibres (1300x). This fibre was not exposed to freezing.

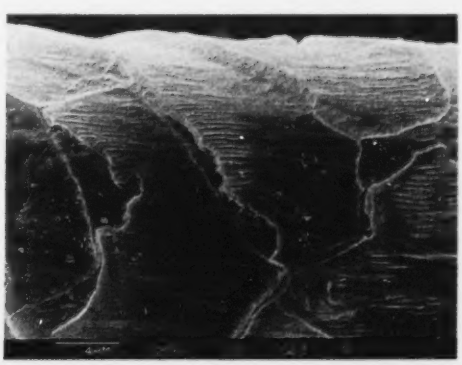

Plate 8. Close-up of the ridges observed on the scales of some coarse wool fibres (3700x). This fibre was exposed to 60 freezing and thawing cycles while wet.

CHAPTER 5 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Summary

The use of freezing in textile conservation is increasing. Wet archaeological textiles and textiles from burial sites are often stored in freezers while awaiting treatment. The use of freezing and thawing to kill insects which infest textile artifacts has proven to be successful (Florian, 1986; Gilberg & Brokerhof, 1991). Recently, Jakes and Mitchell (1992) introduced the use of freezing to slowly dry linen textiles from a marine archaeological site. Textiles are also found frozen in a variety of archaeological contexts. The effects of long term freezing or repeated freezing and thawing on wool textiles have been explored by very few researchers.

This research project was carried out to determine if new, clean wool yarns, whether dry or wet, are damaged by freezing treatments, specifically, cyclical and continuous freezing. Two-ply, unbleached wool yarns were conditioned from the dry state by one of two methods: equilibrated at 65 ± 2% RH and 20 ± 2°C ("dry"), or saturated in distilled water ("wet"). The wool yarns were exposed to two different freezing treatments; 24 hour freeze-thaw cycles for a maximum of 60 cycles, and continuous freezing for a maximum of 60 days. Properties of the wool yarns were evaluated before freezing and after 20, 40, and 60 days, although the changes after 60 days were of primary concern. Prior to testing, all yarns, after removal from the freezer, were air dried at 65 ± 2% RH and 20 ± 2°C, preconditioned at 50°C and reconditioned at 65 ± 2% RH and 20 ± 2°C.

In order to determine whether there were physical and chemical changes in the wool yarns as a result of the freezing treatments a number of properties were measured, including tensile strength, extension at break, energy to break, moisture regain at 11%, 32%, 53%, 65%, 75%, and 97% relative humidity, BET monolayer value, and tributyiphosphine-alcoholic sodium iodide (TASI) solubility. The data were analyzed using a two-way ANOVA with multiple comparisons by Duncan's Multiple Range Test or Scheffé's Test (α=0.05). In addition to the quantitative variables tested by null hypotheses, the qualitative variable of fibre appearance using scanning electron microscopy was considered.

Significant changes in the wool as a result of conditioning and freezing treatments were expected to be evident in the results of the analytical tests. Table 16 summarizes the changes in selected properties of the wool yarns after 60 days of exposure to freezing treatments when comparisons were made with the dry unfrozen control. None of these changes was greater than 5%, nor were they found to be statistically significant. Because these changes were not significant, it was not reasonable to test for correlations to determine how the results of different tests relate to one another. There were some significant changes after 60 days in other properties which were evaluated, such as extension at break, energy at break, and moisture regain at 97% RH; these changes will be briefly discussed. The differences in results between the dry and wet yarns exposed to the same freezing treatments, as well as the differences between cyclically and continuously frozen yarns will also be discussed.

Table 16
Changes[a] in Tensile Strength, Moisture Regain at 65% RH, BET Monolayer, and Solubility of Wool Yarns Exposed to 60 Days/Cycles of Freezing.

Treatment	Tensile Strength % Δ	Moisture Regain at 65% RH % Δ	BET[b] Monolayer % Δ	TASI[c] Solubility % Δ
Freeze-Thaw Dry	+0.3	-2.2	+4.0	-0.9
Freeze-Thaw Wet	+3.3	-2.9	+1.4	-4.1
Continuous Freeze Dry	+2.6	+1.4	-2.4	-0.7
Continuous Freeze Wet	+1.7	-3.3	+3.1	-2.2

Note. None of the changes were determined to be statistically significant.
a % change when compared to the dry unfrozen wool yarns.
b Brunauer-Emmett-Teller monolayer value calculated from Equation 7.
c Tributylphosphine-alcoholic sodium iodide solubility.

Effect of the Length of Freezing Treatment on Changes in Wool

There were no consistent increases or decreases within each set of test results for the wool yarns exposed to each conditioning and freezing procedure as the length of freezing time increased. For example, the moisture regain at 32% RH for the wet wool yarns exposed to continuous freezing for 20 days significantly decreased, then after 60 days, there was a significant increase. This initial significant decrease later followed by a significant increase occurred *only* with the wet continuously frozen yarns, *only* at 32% RH. The reason for this unusual result is not known. This is however, an example of unusual results involving a sample exposed to freezing for 20 days. Other such differences involving the 20 day exposure period occur, but these differences do not consistently involve the same type of conditioning or freezing treatments, nor are they confirmed by the results of the other analytical tests.

Significant changes which occurred did so primarily after extended, 60 day, exposures to the freezing treatment. There were significant increases in extension at break, energy to break, and moisture regain at 97% RH in the wool yarns exposed to 60 days of continuous freezing regardless of whether they were in a wet or dry condition during freezing. These results suggest that there are possibly more amorphous regions in these wool fibres which could allow for easier slippage of molecules when exposed to tensile stresses (Merkel, 1991) and provide more spaces for water molecules to accumulate in at high relative humidities (Watt, 1980). It should be considered, however, that the moisture regain determinations at 97% RH were less reliable than those at other relative humidities.

Exposures for sixty days to cyclical or continuous freezing treatments were found to have no significant effect on the yarn properties of tensile strength, moisture regain at 65% RH, BET monolayer, and TASI solubility. The microscopic appearance of the fibre surface after exposure to freezing treatments did not noticeably change after 60 days. These results may interest textile conservators using brief exposures to freezing and thawing as a method of killing insects, and those using short-term freezer storage prior to treating archaeological textiles.

Effect of Dry vs. Wet Condition of Wool

Significant effects due to the dry or wet condition of the wool were identified in the tensile testing results. It was found that regardless of whether the wool was unfrozen, frozen cyclically or frozen continuously, there were differences in the tensile behavior between all the wool yarns which were dry and all of those which had been wet-out with distilled water. The tensile strength of the yarns which had been wet was 2% lower than the tensile strength of the dry yarns. The extension of these "wet" yarns was 2% higher than that of the dry yarns. These differences, although statistically significant, are relatively minor and not related to freezing exposure. The statistical analysis indicated that there was no interaction between conditioning and freezing treatments on the tensile properties of the wool yarns. The differences in tensile properties between dry and wet wool yarns can not be associated with exposure to freezing; statistically, they are only the result of exposure to wet conditions.

After 60 days of continuous freezing, the moisture regain at 65% RH of the wool yarns frozen while dry (13.97%) was significantly higher than the regain at 65% of those frozen while wet (13.32%); however, the results for both of these conditions are in good agreement with published moisture regain values (eg. 13.6%) (CAN/CGSB-4.2 No. 0-M88). There were no differences in the moisture regain at 65% RH between the dry and wet yarns cyclically frozen for 60 days. Neither the BET monolayer values nor the TASI solubility results differed significantly between the yarns frozen while dry and those frozen while wet.

These results suggest that there is little influence of water content on the changes to the wool fibres exposed to freezing for short periods. Wool fibres will swell when they are exposed to water, increasing up to 18% in diameter (Alexander et al., 1963, p. 87; Maclaren & Milligan, 1981, p. 302). Molecular rearrangement resulting from this swelling leads to an increase in extension and decrease in tensile strength of the yarns (Watt, 1980; Windle, 1956). The results of the BET monolayer determination indicate that there are no significant changes in the water binding sites within the fibres when wool fibres are frozen wet rather than dry. In addition, the solubility results do not suggest changes in the intermolecular bonds within the fibres as a

result of dry or wet condition during freezing. The microscopic appearance of the wool fibres exposed to dry and wet conditions while frozen for 60 days were not noticeably different.

Effect of Cyclical vs. Continuous Freezing on Wool Properties

When tensile strength, extension at break, and energy at break of wool yarns exposed to the same freezing period (0, 20, 40, or 60 days) but different types of freezing (freeze-thaw or continuous) were compared, no statistically significant differences were found. Therefore, whether the wool yarns were cyclically frozen or continuously frozen for up to 60 days, there were no differences in tensile properties.

At 65% RH, there were no significant differences in moisture regain between the wool yarns cyclically frozen and those continuously frozen for 60 days. The yarns frozen and thawed for 60 days while dry had a significantly higher BET monolayer value (6.13%) than the dry wool yarns continuously frozen for 60 days (5.76%). Although statistically significant, this is a difference of only 0.37% moisture and these BET monolayer values are typical of other BET values reported in this study.

There were no differences in TASI solubility after 60 days between the cyclically and continuously frozen yarns. The microscopic appearance of the yarns cyclically frozen for 60 days did not noticeably differ from that of the yarns continuously frozen for 60 days.

These results suggest that when wool yarns are in a sealed environment, the repeated cyclic stress of freezing and thawing has no different effect on the properties of wool fibres when compared to wool which had been continuously frozen for the same length of time. It is likely that damage observed in archaeological textiles, which have been exposed to freezing and thawing cycles while in a northern environment, is caused by other factors such as microorganisms, light, or wind (contributing to desiccation).

Conclusions

Textile conservators may freeze wool artifacts for a variety of reasons. They may store dry or wet textiles in a freezer in order to prevent further deterioration, such as that due to

microorganism growth, prior to conservation treatment. Textiles may be subjected to freezing and thawing cycles as a result of efforts to kill insects. Outside of the textile conservation laboratory, dry or wet wool textiles in archaeological contexts may be exposed to cyclical or continuous freezing for many years. Textiles close to the surface of a northern burial site may be exposed to seasonal freezing and thawing, while those in the permafrost layer of a burial site will remain frozen.

The questions which arise as a result of these situations are: Do freezing treatments cause damage to wool textiles and does the dry or wet condition of the wool influence the effect of the freezing treatments?

The results of this study suggest that after a 60 day period, neither freezing and thawing nor continuous freezing of wool yarns in a dry or wet condition cause significant changes in the physical and chemical properties evaluated. Although the results of extension at break and moisture regain at 97% RH suggest that after continuous freezing for 60 days, regardless of the condition of the wool, there may be an increase in the size or number of amorphous areas within the fibres, the results of the other tests conducted do not strongly support this idea. The microscopic appearance of these fibres suggest no alterations in fibre structure after freezing.

Although there were differences in the tensile strength and extension at break between wool yarns frozen while dry and those exposed to wet conditions, statistical analyses indicated that these differences were not influenced by the freezing treatment. The entire population of wool yarns which had been wet, whether unfrozen or exposed to cyclical or continuous freezing, had significantly lower tensile strength and significantly higher breaking extension than the population of wool yarns which had been dry. These differences are concluded to be a result of exposure to the dry or wet conditions alone rather than the combined effects of conditioning treatments and exposure to freezing.

It can therefore be concluded that cyclical and continuous freezing for up to 60 days have no significant effect on the measured properties of the wool. Whether the wool yarns were dry or wet during freezing, also had no significant effect on the properties which were measured.

Recommendations for Further Research

Through the course of this research project a number of possibilities for further research have arisen. Concerning the test methods used to evaluate changes in the wool following treatment, there is a need to find methods that will provide more precise results. For example, testing of fibre strength rather than yarn strength could be explored. As well, additional chemical tests which may evaluate changes in molecular structure should be sought. References in the literature to such methods are limited and often require highly sensitive but expensive equipment. Sensitive analytical methods could allow for detection of minute changes after short exposures to freezing treatments.

The most commonly used freezing method for the eradication of insects is that recommended by Florian (1986). This method calls for the freezing of the artifacts for 48 hours at -20°C, slow thawing for 8 hours, then immediate refreezing for 48 hours. Due to time restrictions, this experiment was loosely based on Florian's procedure. A future study following Florian's guidelines explicitly and utilizing more precise analytical methods is recommended.

Dry and wet wool yarns remain in a freezer, sealed in freezer storage bags, for future evaluation of the long term effects of continuous freezer storage. It is hoped that these yarns will be tested after they have been frozen for at least 5 years.

Freezing the wool in a completely dry condition may also be considered so that any possible influence of moisture content on the results may be eliminated. It is important to pinpoint any effects of freezing treatment while new wool is wet, conditioned or oven dried before proceeding with new variables. Additional conditions that might be explored include freezing aged wool of known provenance or new wool that has been artificially aged to determine the effects of freezing on weakened or degraded wool. It may also be interesting to evaluate wool which has been frozen while exposed to conditions which are relevant to archaeological situations. Wool could be frozen while exposed to acidic conditions similar to the conditions of peat bogs, saline conditions such as those in marine environments, or while exposed to body fluids such as blood.

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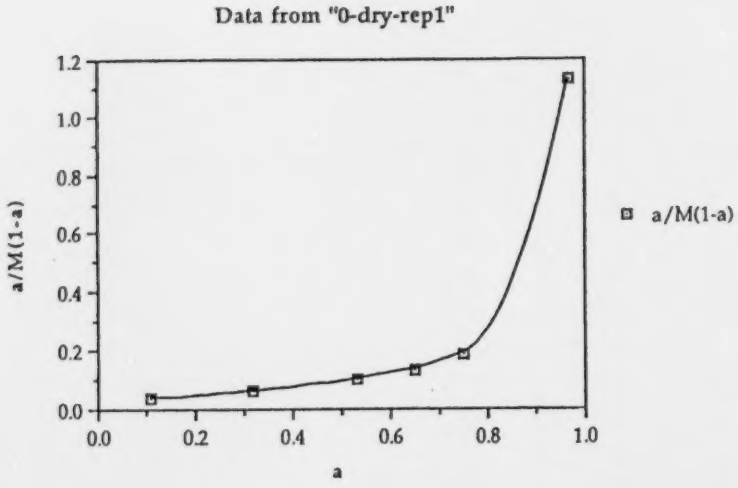
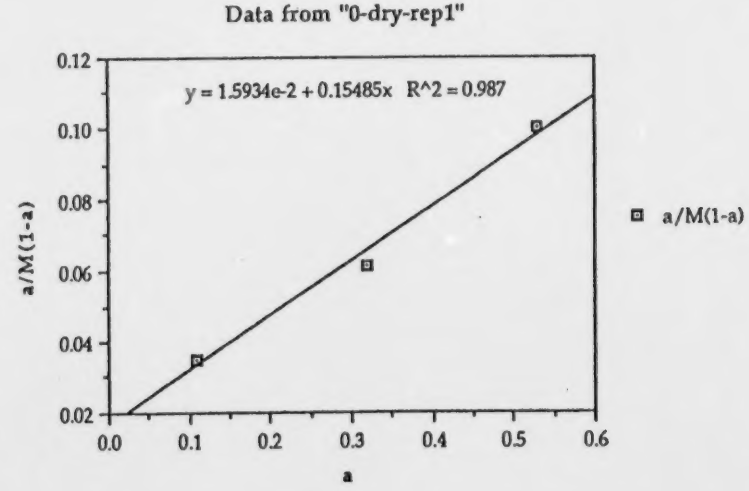
APPENDIX A-1: BET Plots and Monolayer (M_1) Calculations



	RH %	regain %	a	a*-1	(1-a)	M(1-a)	a/M(1-a)	a	a/M(1-a)
1	11	3.52	0.11	-0.110	0.89	3.133	0.035	0.11	0.035
2	32	7.69	0.32	-0.320	0.68	5.229	0.061	0.32	0.061
3	53	11.26	0.53	-0.530	0.47	5.292	0.100	0.53	0.100
4	65	13.82	0.65	-0.650	0.35	4.837	0.134		
5	75	16.14	0.75	-0.750	0.25	4.035	0.186		
6	97	28.57	0.97	-0.970	0.03	0.857	1.132		



$a/M(1-a) = (1/M_1C) + [(C-1)/M_1C]\, a$

$y = 0.015934 + 0.15485\, x$

$y = a/M(1-a)$
$x = a$

$1/M_1C = 0.015934$
$M_1C = 62.75888$

$(C-1)/M_1C = 0.15485$
$(C-1) = 0.15485 \times 62.75888 = 9.7182126$
$C = 10.7182126$

$M_1(10.7182126) = 62.75888$
$M_1 = 5.855$

APPENDIX A-2: Summary Tables of F-Ratios

Yarn Breaking Strength

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: BREAK2

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		175064.75	1163.45	175064.75	2.87	61091.21	1.0	406.0	0.0
UNIV	WET*TYPE	*	81.12	1163.45	6.24	2.87	2.18	13.0	406.0	0.00986
UNIV	GRAND MEAN		175064.75	1163.45	175064.75	2.87	61091.21	1.0	406.0	0.0
UNIV	WET		12.27	1163.45	12.27	2.87	4.28	1.0	406.0	0.03912
UNIV	TYPE		37.65	1163.45	6.27	2.87	2.19	6.0	406.0	0.04314
UNIV	WET*TYPE		31.20	1163.45	5.20	2.87	1.81	6.0	406.0	0.09484
UNIV	CASES(WET,TYPE)	*	1163.45	****	2.87	****	****	406.0	****	****
ERROR TERM: CASES(WET,TYPE)										

Extension at Break

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: EXTENS

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		0.13717E7	10480.18	0.13717E7	25.81	53142.16	1.0	406.0	0.0
UNIV	WET*TYPE	*	998.77	10480.18	76.83	25.81	2.98	13.0	406.0	0.00035
UNIV	GRAND MEAN		0.13717E7	10480.18	0.13717E7	25.81	53142.16	1.0	406.0	0.0
UNIV	WET		116.08	10480.18	116.08	25.81	4.50	1.0	406.0	0.03456
UNIV	TYPE		743.40	10480.18	123.90	25.81	4.80	6.0	406.0	0.00010
UNIV	WET*TYPE		139.29	10480.18	23.22	25.81	0.90	6.0	406.0	0.49523
UNIV	CASES(WET,TYPE)	*	10480.18	****	25.81	****	****	406.0	****	****
ERROR TERM: CASES(WET,TYPE)										

Energy to Break

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: ENERGY2

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		242.47	7.07	242.47	0.02	13927.80	1.0	406.0	0.0
UNIV	WET*TYPE	*	0.40	7.07	0.03	0.02	1.77	13.0	406.0	0.04610
UNIV	GRAND MEAN		242.47	7.07	242.47	0.02	13927.80	1.0	406.0	0.0
UNIV	WET		0.03	7.07	0.03	0.02	1.86	1.0	406.0	0.17333
UNIV	TYPE		0.26	7.07	0.04	0.02	2.49	6.0	406.0	0.02216
UNIV	WET*TYPE		0.11	7.07	0.02	0.02	1.03	6.0	406.0	0.40835
UNIV	CASES(WET,TYPE)	*	7.07	****	0.02	****	****	406.0	****	****
ERROR TERM: CASES(WET,TYPE)										

Moisture Regain at 11% RH

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: P11

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		466.13	0.18	466.13	0.6261E-2	74439.57	1.0	28.0	.168E-48
UNIV	WET*TYPE	*	2.10	0.18	0.16	0.6261E-2	25.84	13.0	28.0	.364E-11
UNIV	GRAND MEAN		466.13	0.18	466.13	0.6261E-2	74439.57	1.0	28.0	.168E-48
UNIV	WET		0.02	0.18	0.02	0.6261E-2	3.65	1.0	28.0	0.06630
UNIV	TYPE		1.44	0.18	0.24	0.6261E-2	38.31	6.0	28.0	.307E-11
UNIV	WET*TYPE		0.64	0.18	0.11	0.6261E-2	17.07	6.0	28.0	0.340E-7
UNIV	CASES(WET,TYPE)	*	0.18	****	0.6261E-2	****	****	28.0	****	****
ERROR TERM: CASES(WET,TYPE)										

Moisture Regain at 32% RH

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: P32

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		2366.70	0.11	2366.70	0.3854E-2	613968.37	1.0	28.0	0.0
UNIV	WET*TYPE	*	2.82	0.11	0.22	0.3854E-2	56.27	13.0	28.0	.152E-15
UNIV	GRAND MEAN		2366.70	0.11	2366.70	0.3854E-2	613968.37	1.0	28.0	0.0
UNIV	WET		0.33	0.11	0.33	0.3854E-2	86.40	1.0	28.0	0.471E-9
UNIV	TYPE		1.69	0.11	0.28	0.3854E-2	73.22	6.0	28.0	.821E-15
UNIV	WET*TYPE		0.79	0.11	0.13	0.3854E-2	34.30	6.0	28.0	.118E-10
UNIV	CASES(WET,TYPE)	*	0.11	****	0.3854E-2	****	****	28.0	****	****
ERROR TERM: CASES(WET,TYPE)										

Moisture Regain at 53% RH

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: P53

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		5231.81	0.48	5231.81	0.02	303251.36	1.0	28.0	0.0
UNIV	WET*TYPE	*	2.31	0.48	0.18	0.02	10.30	13.0	28.0	0.175E-6
UNIV	GRAND MEAN		5231.81	0.48	5231.81	0.02	303251.36	1.0	28.0	0.0
UNIV	WET		0.03	0.48	0.03	0.02	1.99	1.0	28.0	0.16963
UNIV	TYPE		1.02	0.48	0.17	0.02	9.85	6.0	28.0	0.743E-5
UNIV	WET*TYPE		1.26	0.48	0.21	0.02	12.14	6.0	28.0	0.106E-5
UNIV	CASES(WET,TYPE)	*	0.48	****	0.02	****	****	28.0	****	****
ERROR TERM: CASES(WET,TYPE)										

Moisture Regain at 65% RH

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: P65

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		7607.32	0.39	7607.32	0.01	544862.83	1.0	28.0	0.0
UNIV	WET*TYPE	*	2.14	0.39	0.16	0.01	11.79	13.0	28.0	0.401E-7
UNIV	GRAND MEAN		7607.32	0.39	7607.32	0.01	544862.83	1.0	28.0	0.0
UNIV	WET		0.03	0.39	0.03	0.01	2.26	1.0	28.0	0.14435
UNIV	TYPE		1.26	0.39	0.21	0.01	15.02	6.0	28.0	0.128E-6
UNIV	WET*TYPE		0.85	0.39	0.14	0.01	10.16	6.0	28.0	0.560E-5
UNIV	CASES(WET,TYPE)	*	0.39	****	0.01	****	****	28.0	****	****
ERROR TERM: CASES(WET,TYPE)										

Moisture Regain at 75% RH

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: P75

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		10660.99	0.39	10660.99	0.01	772269.27	1.0	28.0	0.0
UNIV	WET*TYPE	*	1.12	0.39	0.09	0.01	6.23	13.0	28.0	0.00003
UNIV	GRAND MEAN		10660.99	0.39	10660.99	0.01	772269.27	1.0	28.0	0.0
UNIV	WET		0.01	0.39	0.01	0.01	0.77	1.0	28.0	0.38640
UNIV	TYPE		0.44	0.39	0.07	0.01	5.37	6.0	28.0	0.00086
UNIV	WET*TYPE		0.66	0.39	0.11	0.01	8.01	6.0	28.0	0.00004
UNIV	CASES(WET,TYPE)	*	0.39	****	0.01	****	****	28.0	****	****
ERROR TERM: CASES(WET,TYPE)										

Moisture Regain at 97% RH

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: P97

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		36115.79	5.95	36115.79	0.21	169884.33	1.0	28.0	0.0
UNIV	WET*TYPE	*	7.33	5.95	0.56	0.21	2.65	13.0	28.0	0.01486
UNIV	GRAND MEAN		36115.79	5.95	36115.79	0.21	169884.33	1.0	28.0	0.0
UNIV	WET		0.01	5.95	0.01	0.21	0.05	1.0	28.0	0.82937
UNIV	TYPE		6.05	5.95	1.01	0.21	4.74	6.0	28.0	0.00189
UNIV	WET*TYPE		1.27	5.95	0.21	0.21	1.00	6.0	28.0	0.44735
UNIV	CASES(WET,TYPE)	*	5.95	****	0.21	****	****	28.0	****	****
ERROR TERM: CASES(WET,TYPE)										

BET Monolayer Value

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: BET

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		1450.13	0.20	1450.13	0.7152E-2	202747.35	1.0	28.0	0.0
UNIV	WET*TYPE	*	1.00	0.20	0.08	0.7152E-2	10.70	13.0	28.0	0.115E-6
UNIV	GRAND MEAN		1450.13	0.20	1450.13	0.7152E-2	202747.35	1.0	28.0	0.0
UNIV	WET		0.06	0.20	0.06	0.7152E-2	7.79	1.0	28.0	0.00934
UNIV	TYPE		0.52	0.20	0.09	0.7152E-2	12.19	6.0	28.0	0.102E-5
UNIV	WET*TYPE		0.42	0.20	0.07	0.7152E-2	9.71	6.0	28.0	0.843E-5
UNIV	CASES(WET,TYPE)	*	0.20	****	0.7152E-2	****	****	28.0	****	****
ERROR TERM: CASES(WET,TYPE)										

Tributylphosphine-Alcoholic Sodium Iodide Solubility

HIERARCHICAL SUMMARY TABLE OF F-RATIOS FOR: PVAL

TYPE	PART OF MODEL		SSH	SSE	MSH	MSE	F-RATIO	DFH	DFE	PROB
UNIV	GRAND MEAN		53534.27	2.69	53534.27	0.19	278803.56	1.0	14.0	.168E-30
UNIV	WET*TYPE	*	21.89	2.69	1.68	0.19	8.77	13.0	14.0	0.00013
UNIV	GRAND MEAN		53534.27	2.69	53534.27	0.19	278803.56	1.0	14.0	.168E-30
UNIV	WET		0.12	2.69	0.12	0.19	0.63	1.0	14.0	0.44070
UNIV	TYPE		10.67	2.69	1.78	0.19	9.26	6.0	14.0	0.00033
UNIV	WET*TYPE		11.10	2.69	1.85	0.19	9.63	6.0	14.0	0.00027
UNIV	CASES(WET,TYPE)	*	2.69	****	0.19	****	****	14.0	****	****
ERROR TERM: CASES(WET,TYPE)										

APPENDIX A-3: Raw Data

Yarn Tensile Testing Raw Data

Sample: No Freeze-dry

Gauge Length: 125 mm
TestSpeed 220 mm/60s
Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	2.034	20.0	66.65	53.3	74.31	0.7290	18.2
2	2.110	20.7	66.20	53.0	73.01	0.7162	18.1
3	1.984	19.5	67.28	53.8	70.49	0.6915	18.3
4	2.038	20.0	67.59	54.1	68.24	0.6694	18.4
5	1.985	19.5	63.93	51.1	64.14	0.6292	17.4
6	2.090	20.5	70.56	56.4	81.89	0.8033	19.2
7	1.926	18.9	69.25	55.4	74.50	0.7308	18.9
8	2.176	21.3	67.06	53.6	73.04	0.7165	18.3
9	1.978	19.4	72.98	58.4	78.98	0.7748	19.9
10	2.184	21.4	70.19	56.2	69.84	0.6851	19.1
11	1.965	19.3	56.94	45.6	48.62	0.4770	15.5
12	1.905	18.7	72.30	57.8	65.64	0.6439	19.7
13	2.067	20.3	66.56	53.2	75.94	0.7450	18.2
14	1.902	18.7	64.78	51.8	58.12	0.5702	17.7
15	2.140	21.0	76.03	60.8	88.38	0.8670	20.7
16	2.083	20.4	72.79	58.2	79.39	0.7788	19.9
17	1.995	19.6	73.75	59.0	80.49	0.7896	20.1
18	2.035	20.0	76.30	61.0	84.57	0.8296	20.8
19	2.015	19.8	63.57	50.9	62.33	0.6115	17.3
20	2.063	20.2	69.43	55.5	73.66	0.7226	18.9
21	2.278	22.3	74.34	59.5	89.59	0.8789	20.3
22	2.421	23.8	78.75	63.0	104.70	1.0271	21.5
23	2.052	20.1	69.10	55.3	76.78	0.7532	18.8
24	2.025	19.9	65.94	52.8	68.03	0.6674	18.0
25	2.056	20.2	60.00	48.0	53.03	0.5202	16.4
26	1.777	17.4	62.39	49.9	53.17	0.5216	17.0
27	2.127	20.9	80.46	64.4	94.01	0.9222	21.9
28	2.020	19.8	72.21	57.8	81.60	0.8005	19.7
29	2.110	20.7	71.67	57.3	80.46	0.7893	19.5
30	2.459	24.1	70.53	56.4	85.42	0.8380	19.2
MEAN	2.07	20.3	69.3	55.5	74.4	0.7300	18.9
Std Dev	0.140	1.367	5.326	4.257	12.419	0.1218	1.450

*Note: Nm = kgf mm/A x 0.00981

Sample: No Freeze-wet

Gauge Length: 125 mm
TestSpeed 220 mm/60s
Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	2.046	20.1	73.79	59.0	80.79	0.7925	20.1
2	2.060	20.2	67.77	54.2	72.43	0.7105	18.5
3	2.051	20.1	77.50	62.0	89.74	0.8803	21.1
4	1.954	19.2	84.43	67.5	85.46	0.8384	23.0
5	1.909	18.7	72.65	58.1	71.79	0.7043	19.8
6	2.030	19.9	73.50	58.8	76.52	0.7507	20.0
7	1.825	17.9	69.59	55.7	64.64	0.6341	19.0
8	1.964	19.3	71.08	56.9	70.70	0.6936	19.4
9	1.999	19.6	70.17	56.1	73.46	0.7206	19.1
10	2.185	21.4	74.63	59.7	86.78	0.8513	20.4
11	2.174	21.3	80.13	64.1	93.54	0.9176	21.9
12	1.850	18.1	60.29	48.2	53.31	0.5230	16.4
13	2.168	21.3	78.67	62.9	91.82	0.9008	21.5
14	2.016	19.8	71.30	57.0	73.25	0.7186	19.4
15	2.113	20.7	67.66	54.1	74.66	0.7324	18.5
16	1.977	19.4	68.77	55.0	71.28	0.6993	18.8
17	1.988	19.5	64.59	51.7	69.50	0.6818	17.6
18	2.287	22.4	68.99	55.2	81.10	0.7956	18.8
19	2.314	22.7	67.85	54.3	83.73	0.8214	18.5
20	2.118	20.8	70.09	56.1	82.61	0.8104	19.1
21	2.105	20.7	67.56	54.0	70.81	0.6946	18.4
22	1.942	19.1	73.12	58.5	78.38	0.7689	19.9
23	2.201	21.6	73.61	58.9	86.10	0.8446	20.1
24	2.091	20.5	71.19	57.0	78.34	0.7685	19.4
25	2.225	21.8	68.03	54.4	72.98	0.7159	18.6
26	1.867	18.3	64.80	51.8	59.28	0.5815	17.7
27	2.436	23.9	78.67	62.9	91.47	0.8973	21.5
28	1.997	19.6	80.31	64.2	79.43	0.7792	21.9
29	1.974	19.4	65.28	52.2	63.41	0.6221	17.8
30	2.024	19.9	67.64	54.1	75.15	0.7372	18.4
MEAN	2.06	20.2	71.5	57.2	76.7	0.7529	19.5
Std Dev	0.141	1.383	5.409	4.323	9.667	0.0948	1.480

*Note: Nm = kgf mm/A x 0.00981

Tensile Raw Data (cont.)

Sample: 20 freeze-thaw - dry

Gauge Length: 125 mm
TestSpeed 220 mm/60s

Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	2.225	21.8	84.03	67.2	91.46	0.8972	22.9
2	2.062	20.2	76.00	60.8	81.96	0.8040	20.7
3	2.353	23.1	79.58	63.7	91.98	0.9023	21.7
4	2.021	19.8	70.15	56.1	77.13	0.7566	19.1
5	2.219	21.8	67.63	54.1	77.69	0.7621	18.4
6	1.780	17.5	57.21	45.8	51.24	0.5027	15.6
7	1.800	17.7	64.77	51.8	60.60	0.5945	17.7
8	1.824	17.9	58.32	46.7	54.59	0.5355	15.9
9	1.803	17.7	64.00	51.2	62.39	0.6120	17.5
10	1.989	19.5	71.52	57.2	67.13	0.6585	19.5
11	2.007	19.7	68.99	55.2	71.51	0.7015	18.8
12	2.397	23.5	88.71	71.0	109.90	1.0781	24.2
13	1.927	18.9	70.20	56.2	61.69	0.6052	19.1
14	2.285	22.4	76.46	61.2	91.70	0.8996	20.9
15	1.970	19.3	78.40	62.7	86.06	0.8442	21.4
16	1.915	18.8	65.36	52.3	62.05	0.6087	17.8
17	2.374	23.3	83.91	67.1	105.20	1.0320	22.9
18	2.043	20.0	72.46	58.0	69.49	0.6817	19.8
19	1.879	18.4	65.38	52.3	66.35	0.6509	17.8
20	2.109	20.7	76.94	61.6	78.63	0.7714	21.0
21	1.846	18.1	65.64	52.5	54.61	0.5357	17.9
22	1.936	19.0	67.12	53.7	66.93	0.6566	18.3
23	1.961	19.2	71.84	57.5	77.17	0.7570	19.6
24	2.258	22.2	71.14	56.9	81.00	0.7946	19.4
25	2.403	23.6	77.05	61.6	90.34	0.8862	21.0
26	2.059	20.2	75.97	60.8	86.94	0.8529	20.7
27	2.173	21.3	71.27	57.0	79.85	0.7833	19.4
28	2.289	22.5	78.52	62.8	96.06	0.9423	21.4
29	2.160	21.2	81.27	65.0	88.49	0.8681	22.2
30	1.805	17.7	68.25	54.6	61.62	0.6045	18.6
MEAN	2.06	20.2	72.3	57.8	76.7	0.7527	19.7
Std Dev	0.197	1.938	7.467	5.970	15.170	0.1488	2.041

*Note: Nm = kgf mm/A x 0.00981

Sample: 20 freeze-thaw - wet

Gauge Length: 125 mm
TestSpeed 220 mm/60s

Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	2.113	20.7	72.92	58.3	79.23	0.7772	19.9
2	2.062	20.2	80.84	64.7	83.88	0.8229	22.0
3	1.964	19.3	68.80	55.0	74.86	0.7344	18.8
4	2.079	20.4	77.79	62.2	83.36	0.8178	21.2
5	1.948	19.1	72.32	57.9	75.45	0.7402	19.7
6	2.146	21.1	78.78	63.0	89.92	0.8821	21.5
7	2.083	20.4	69.28	55.4	73.46	0.7206	18.9
8	2.115	20.7	80.43	64.3	88.01	0.8634	21.9
9	2.264	22.2	80.31	64.2	96.17	0.9434	21.9
10	2.285	22.4	71.92	57.5	87.83	0.8616	19.6
11	2.196	21.5	76.77	61.4	87.99	0.8632	20.9
12	2.015	19.8	72.73	58.2	78.82	0.7732	19.8
13	1.957	19.2	63.04	50.4	66.90	0.6563	17.2
14	2.374	23.3	77.93	62.3	93.45	0.9167	21.3
15	2.068	20.3	76.87	61.5	89.77	0.8806	21.0
16	2.172	21.3	77.31	61.8	90.17	0.8846	21.1
17	2.034	20.0	68.18	54.5	71.95	0.7058	18.6
18	2.034	20.0	73.94	59.2	82.03	0.8047	20.2
19	2.102	20.6	71.86	57.5	76.94	0.7548	19.6
20	1.913	18.8	64.92	51.9	65.62	0.6437	17.7
21	2.121	20.8	73.05	58.4	73.31	0.7192	19.9
22	1.997	19.6	73.50	58.8	79.37	0.7786	20.0
23	2.009	19.7	65.76	52.6	68.07	0.6678	17.9
24	1.968	19.3	73.05	58.4	77.07	0.7561	19.9
25	2.174	21.3	88.35	70.7	95.31	0.9350	24.1
26	1.887	18.5	65.98	52.8	66.61	0.6534	18.0
27	2.323	22.8	79.14	63.3	104.80	1.0281	21.6
28	2.004	19.7	82.40	65.9	88.51	0.8683	22.5
29	1.703	16.7	67.98	54.4	60.86	0.5970	18.5
30	2.191	21.5	70.20	56.2	79.52	0.7801	19.1
MEAN	2.08	20.4	73.9	59.1	81.0	0.7944	20.1
Std Dev	0.140	1.365	5.858	4.687	10.404	0.1021	1.601

*Note: Nm = kgf mm/A x 0.00981

Tensile Raw Data (cont.)

Sample: 20 days-continuous freeze-dry

Gauge Length: 125 mm
TestSpeed 220 mm/60s

Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	1.839	18.0	71.31	57.0	61.71	0.6054	19.4
2	1.663	16.3	58.71	47.0	42.48	0.4167	16.0
3	1.753	17.2	63.90	51.1	56.05	0.5499	17.4
4	2.072	20.3	78.41	62.7	78.37	0.7688	21.4
5	2.044	20.1	70.11	56.1	72.15	0.7078	19.1
6	1.902	18.7	69.99	56.0	64.88	0.6365	19.1
7	1.872	18.4	60.74	48.6	53.15	0.5214	16.6
8	2.024	19.9	63.16	50.5	69.18	0.6787	17.2
9	2.174	21.3	68.20	54.6	69.20	0.6789	18.6
10	2.048	20.1	76.51	61.2	78.28	0.7679	20.9
11	1.905	18.7	75.32	60.3	69.77	0.6844	20.5
12	1.933	19.0	68.25	54.6	66.49	0.6523	18.6
13	2.017	19.8	70.05	56.0	69.21	0.6790	19.1
14	2.136	21.0	78.59	62.9	86.09	0.8445	21.4
15	1.960	19.2	75.70	60.6	72.32	0.7095	20.6
16	2.007	19.7	70.23	56.2	75.41	0.7398	19.2
17	2.110	20.7	68.03	54.4	73.37	0.7198	18.6
18	2.470	24.2	73.57	58.9	94.33	0.9254	20.1
19	1.993	19.6	69.98	56.0	71.71	0.7035	19.1
20	2.089	20.5	66.75	53.4	68.75	0.6744	18.2
21	2.235	21.9	72.32	57.9	80.89	0.7935	19.7
22	2.149	21.1	83.10	66.5	90.51	0.8879	22.7
23	2.239	22.0	81.67	65.3	96.00	0.9418	22.3
24	2.275	22.3	93.55	74.8	105.70	1.0369	25.5
25	2.103	20.6	72.06	57.6	78.59	0.7710	19.7
26	2.070	20.3	67.01	53.6	68.85	0.6754	18.3
27	1.919	18.8	70.27	56.2	74.03	0.7262	19.2
28	2.071	20.3	66.01	52.8	71.13	0.6978	18.0
29	2.275	22.3	70.34	56.3	85.57	0.8394	19.2
30	1.952	19.1	77.37	61.9	83.34	0.8176	21.1
MEAN	2.04	20.0	71.7	57.4	74.3	0.7284	19.6
Std Dev	0.166	1.626	7.057	5.642	12.933	0.1269	1.925

*Note: Nm = kgf mm/A x 0.00981

Sample: 20 days-continuous freeze-wet

Gauge Length: 125 mm
TestSpeed 220 mm/60s

Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	2.348	23.0	70.03	56.0	81.68	0.8013	19.1
2	1.895	18.6	65.51	52.4	65.98	0.6473	17.9
3	2.044	20.1	73.44	58.8	82.81	0.8124	20.0
4	2.350	23.1	75.27	60.2	94.78	0.9298	20.5
5	1.923	18.9	66.49	53.2	64.41	0.6319	18.1
6	1.785	17.5	76.31	61.0	66.25	0.6499	20.8
7	2.301	22.6	77.90	62.3	97.42	0.9557	21.2
8	2.225	21.8	70.49	56.4	84.85	0.8324	19.2
9	1.980	19.4	61.59	49.3	58.84	0.5772	16.8
10	2.372	23.3	67.44	54.0	84.61	0.8300	18.4
11	2.040	20.0	64.63	51.7	68.54	0.6724	17.6
12	2.036	20.0	68.58	54.9	68.94	0.6763	18.7
13	1.977	19.4	79.00	63.2	75.99	0.7455	21.5
14	2.051	20.1	73.79	59.0	79.99	0.7847	20.1
15	1.977	19.4	75.48	60.4	79.81	0.7829	20.6
16	2.079	20.4	72.22	57.8	74.54	0.7312	19.7
17	1.783	17.5	69.68	55.7	67.73	0.6644	19.0
18	1.745	17.1	69.84	55.9	60.42	0.5927	19.0
19	2.095	20.6	76.00	60.8	89.69	0.8799	20.7
20	1.730	17.0	63.34	50.7	53.63	0.5261	17.3
21	2.231	21.9	77.71	62.2	93.26	0.9149	21.2
22	1.941	19.0	76.52	61.2	71.72	0.7036	20.9
23	2.118	20.8	76.01	60.8	88.62	0.8694	20.7
24	2.024	19.9	63.60	50.9	65.95	0.6470	17.3
25	1.729	17.0	66.67	53.3	64.63	0.6340	18.2
26	1.674	16.4	63.96	51.2	48.08	0.4717	17.4
27	2.123	20.8	82.52	66.0	89.72	0.8802	22.5
28	1.719	16.9	60.73	48.6	53.24	0.5223	16.6
29	1.927	18.9	72.17	57.7	71.31	0.6996	19.7
30	1.925	18.9	65.13	52.1	58.46	0.5735	17.8
MEAN	2.00	19.7	70.7	56.6	73.5	0.7213	19.3
Std Dev	0.199	1.956	5.798	4.630	13.316	0.1306	1.575

*Note: Nm = kgf mm/A x 0.00981

Tensile Raw Data (cont.)

Sample: 40 freeze-thaw - dry

Gauge Length: 125 mm
Test Spee 220 mm/60s
Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Peak Energy (kgf mm/A)	Energy (Nm or J)	Break Time (s)
1	2.038	20.0	61.60	49.3	62.71	0.6152	16.8
2	2.071	20.3	64.39	51.5	70.27	0.6893	17.6
3	2.216	21.7	69.65	55.7	71.04	0.6969	19.0
4	2.325	22.8	60.04	48.0	71.76	0.7040	16.4
5	2.442	24.0	82.88	66.3	109.5	1.0742	22.6
6	2.251	22.1	74.71	59.8	91.94	0.9019	20.4
7	2.079	20.4	75.49	60.4	85.32	0.8370	20.6
8	2.272	22.3	67.48	54.0	74.23	0.7282	18.4
9	1.965	19.3	56.59	45.3	54.17	0.5314	15.4
10	2.050	20.1	62.77	50.2	61.75	0.6058	17.1
11	2.050	20.1	69.07	55.3	68.74	0.6743	18.8
12	2.122	20.8	59.16	47.3	62.13	0.6095	16.1
13	2.385	23.4	74.20	59.4	87.65	0.8598	20.2
14	2.007	19.7	75.40	60.3	84.52	0.8291	20.6
15	2.136	21.0	68.18	54.5	78.45	0.7696	18.6
16	2.212	21.7	70.30	56.2	80.89	0.7935	19.2
17	2.078	20.4	75.41	60.3	79.63	0.7812	20.6
18	2.134	20.9	70.38	56.3	79.21	0.7771	19.2
19	1.793	17.6	65.28	52.2	52.88	0.5188	17.8
20	2.224	21.8	74.41	59.5	88.42	0.8674	20.3
21	1.992	19.5	70.85	56.7	74.38	0.7297	19.3
22	2.176	21.3	71.01	56.8	79.52	0.7801	19.4
23	1.997	19.6	62.89	50.3	59.92	0.5878	17.2
24	2.075	20.4	81.45	65.2	83.81	0.8222	22.2
25	2.415	23.7	79.93	63.9	92.70	0.9094	21.8
26	2.109	20.7	66.27	53.0	75.27	0.7384	18.1
27	2.417	23.7	76.08	60.9	95.29	0.9348	20.7
28	2.079	20.4	76.27	61.0	86.01	0.8438	20.8
29	2.148	21.1	73.09	58.5	77.96	0.7648	19.9
30	2.260	22.2	65.84	52.7	68.54	0.6724	18.0
MEAN	2.15	21.1	70.0	56.0	76.95	0.7549	19.1
Std Dev	0.151	1.478	6.687	5.353	12.747	0.1250	1.823

*Note: Nm = kgf mm/A x 0.00981

Sample: 40 freeze-thaw - wet

Gauge Length: 125 mm
Test Spee 220 mm/60s
Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Peak Energy (kgf mm/A)	Energy (Nm or J)	Break Time (s)
1	1.941	19.0	67.95	54.4	70.38	0.6904	18.5
2	1.893	18.6	74.48	59.6	60.28	0.5913	20.3
3	2.117	20.8	78.62	62.9	94.38	0.9259	21.4
4	2.090	20.5	75.72	60.6	91.44	0.8970	20.7
5	1.887	18.5	71.86	57.5	74.49	0.7307	19.6
6	1.693	16.6	54.55	43.6	44.84	0.4399	14.9
7	2.141	21.0	77.90	62.3	91.47	0.8973	21.2
8	1.981	19.4	79.80	63.8	89.09	0.8740	21.8
9	2.047	20.1	66.51	53.2	70.83	0.6948	18.1
10	1.851	18.2	63.93	51.1	62.47	0.6128	17.4
11	2.003	19.6	69.46	55.6	74.12	0.7271	18.9
12	1.843	18.1	67.19	53.8	61.49	0.6032	18.3
13	1.893	18.6	64.17	51.3	61.63	0.6046	17.5
14	2.055	20.2	69.25	55.4	76.68	0.7522	18.9
15	2.083	20.4	74.52	59.6	79.22	0.7771	20.3
16	1.706	16.7	58.68	46.9	47.75	0.4684	16.0
17	1.903	18.7	65.40	52.3	68.24	0.6694	17.8
18	2.180	21.4	76.00	60.8	92.37	0.9061	20.7
19	2.168	21.3	76.50	61.2	93.12	0.9135	20.9
20	2.156	21.2	67.40	53.9	74.15	0.7274	18.4
21	1.913	18.8	59.38	47.5	57.36	0.5627	16.2
22	2.067	20.3	67.37	53.9	78.87	0.7737	18.4
23	2.123	20.8	66.30	53.0	76.32	0.7487	18.1
24	1.977	19.4	58.90	47.1	57.76	0.5666	16.1
25	2.542	24.9	72.62	58.1	96.40	0.9457	19.8
26	2.527	24.8	85.08	68.1	116.1	1.1389	23.2
27	2.046	20.1	62.97	50.4	68.61	0.6731	17.2
28	2.038	20.0	75.65	60.5	79.89	0.7837	20.6
29	1.808	17.7	64.78	51.8	63.20	0.6200	17.7
30	1.926	18.9	74.60	59.7	71.23	0.6988	20.3
MEAN	2.02	19.8	69.6	55.7	74.8	0.7338	19.0
Std Dev	0.190	1.866	7.177	5.751	15.788	0.1549	1.951

*Note: Nm = kgf mm/A x 0.00981

Tensile Raw Data (cont.)

Sample: 40 days - continuous freeze - dry

Gauge Length: 125 mm
Test Spee: 220 mm/60s
Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Peak Energy (kgf mm/A)	Energy (Nm or J)	Break Time (s)
1	2.150	21.1	74.93	59.9	88.60	0.8692	20.4
2	2.344	23.0	79.95	64.0	97.81	0.9595	21.8
3	2.274	22.3	70.69	56.6	85.96	0.8433	19.3
4	2.193	21.5	68.47	54.8	88.53	0.8685	18.7
5	2.238	22.0	69.42	55.5	79.53	0.7802	18.9
6	2.236	21.9	64.95	52.0	74.47	0.7306	17.7
7	2.305	22.6	74.66	59.7	87.96	0.8629	20.4
8	2.463	24.2	76.62	61.3	105.2	1.0320	20.9
9	1.991	19.5	61.96	49.6	68.24	0.6694	16.9
10	2.349	23.0	67.55	54.0	85.09	0.8347	18.4
11	2.098	20.6	64.40	51.5	75.50	0.7407	17.6
12	2.207	21.7	73.94	59.2	89.27	0.8757	20.2
13	2.068	20.3	60.15	48.1	62.82	0.6163	16.4
14	2.001	19.6	63.70	51.0	73.00	0.7161	17.4
15	2.134	20.9	67.04	53.6	76.01	0.7457	18.3
16	1.879	18.4	54.59	43.7	45.10	0.4424	14.9
17	1.895	18.6	70.64	56.5	66.46	0.6520	19.3
18	2.152	21.1	60.81	48.6	66.90	0.6563	16.6
19	2.056	20.2	74.77	59.8	76.90	0.7544	20.4
20	2.169	21.3	69.02	55.2	67.94	0.6665	18.8
21	2.068	20.3	66.34	53.1	65.49	0.6425	18.1
22	2.074	20.3	72.65	58.1	82.64	0.8107	19.8
23	2.287	22.4	63.24	50.6	74.40	0.7299	17.2
24	2.091	20.5	74.33	59.5	82.45	0.8088	20.3
25	2.164	21.2	65.88	52.7	77.57	0.7610	18.0
26	2.169	21.3	79.85	63.9	92.93	0.9116	21.8
27	1.989	19.5	65.50	52.4	67.79	0.6650	17.9
28	2.348	23.0	66.46	53.2	85.57	0.8394	18.1
29	2.195	21.5	70.64	56.5	83.76	0.8217	19.3
30	2.152	21.1	58.79	47.0	61.46	0.6029	16.0
MEAN	2.16	21.2	68.4	54.7	77.8	0.7637	18.7
Std Dev	0.136	1.342	6.179	4.946	12 337	0.1210	1.689

*Note: Nm = kgf mm/A x 0.00981

Sample: 40 days - continuous freeze - wet

Gauge Length: 125 mm
Test Spee: 220 mm/60s
Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Peak Energy (kgf mm/A)	Energy (Nm or J)	Break Time (s)
1	2.059	20.2	71.93	57.5	77.60	0.7613	19.6
2	2.066	20.3	73.89	59.1	82.78	0.8121	20.2
3	2.302	22.6	69.71	55.8	84.99	0.8338	19.0
4	2.036	20.0	64.95	52.0	65.46	0.6422	17.7
5	2.071	20.3	69.22	55.4	81.23	0.7969	18.9
6	1.909	18.7	60.69	48.6	58.45	0.5734	16.6
7	2.123	20.8	73.21	58.6	81.90	0.8034	20.0
8	1.879	18.4	74.57	59.7	78.21	0.7672	20.3
9	1.978	19.4	75.84	60.7	77.09	0.7563	20.7
10	1.883	18.5	61.10	48.9	56.24	0.5517	16.7
11	2.427	23.8	75.47	60.4	87.40	0.8574	20.6
12	1.753	17.2	62.42	49.9	53.16	0.5215	17.0
13	2.358	23.1	78.14	62.5	99.57	0.9768	21.3
14	1.846	18.1	63.21	50.6	62.62	0.6143	17.2
15	2.132	20.9	73.59	58.9	84.39	0.8279	20.1
16	2.463	24.2	82.77	66.2	108.3	1.0624	22.6
17	1.838	18.0	67.29	53.8	64.33	0.6311	18.4
18	2.035	20.0	60.60	48.5	62.33	0.6115	16.5
19	2.153	21.1	68.14	54.5	73.21	0.7182	18.6
20	1.804	17.7	64.52	51.6	63.52	0.6231	17.6
21	2.067	20.3	76.32	61.1	78.80	0.7730	20.8
22	2.079	20.4	75.42	60.3	80.80	0.7926	20.6
23	2.071	20.3	63.68	50.9	69.37	0.6805	17.4
24	2.191	21.5	69.00	55.2	83.29	0.8171	18.8
25	2.090	20.5	75.82	60.7	83.87	0.8228	20.7
26	1.957	19.2	72.58	58.1	74.07	0.7266	19.8
27	2.024	19.9	65.58	52.5	75.54	0.7410	17.9
28	1.862	18.3	63.96	51.2	58.42	0.5731	17.4
29	2.094	20.5	70.94	56.8	81.88	0.8032	19.3
30	2.111	20.7	68.58	54.9	76.35	0.7490	18.7
MEAN	2.06	20.2	69.8	55.8	75.5	0.7407	19.0
Std Dev	0.175	1.715	5.841	4.672	12.490	0.1225	1.597

*Note: Nm = kgf mm/A x 0.00981

Tensile Raw Data (cont.)

Sample: 60 freeze-thaw - dry

Gauge Length: 125 mm
TestSpeed: 220 mm/60s
Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	2.064	20.2	78.96	63.2	88.75	0.8706	21.5
2	2.258	22.2	78.33	62.7	83.04	0.8146	21.4
3	2.082	20.4	68.14	54.5	76.43	0.7498	18.6
4	2.017	19.8	76.39	61.1	73.67	0.7227	20.8
5	1.894	18.6	68.56	54.8	60.76	0.5961	18.7
6	2.197	21.6	72.98	58.4	85.55	0.8392	19.9
7	2.295	22.5	76.36	61.1	94.02	0.9223	20.8
8	1.944	19.1	64.92	51.9	67.24	0.6596	17.7
9	1.965	19.3	73.69	59.0	74.75	0.7333	20.1
10	2.117	20.8	72.70	58.2	80.08	0.7856	19.8
11	1.894	18.6	69.76	55.8	64.92	0.6369	19.0
12	2.050	20.1	74.89	59.9	83.40	0.8182	20.4
13	1.974	19.4	58.68	46.9	55.55	0.5449	16.0
14	2.105	20.7	80.04	64.0	86.73	0.8508	21.8
15	2.089	20.5	70.14	56.1	72.66	0.7128	19.1
16	1.901	18.6	69.41	55.5	62.24	0.6106	18.9
17	2.666	26.2	78.92	63.1	104.9	1.0291	21.5
18	1.831	18.0	71.77	57.4	68.55	0.6725	19.6
19	2.411	23.7	75.11	60.1	93.24	0.9147	20.5
20	2.212	21.7	71.29	57.0	84.23	0.8263	19.4
21	1.800	17.7	61.69	49.4	55.28	0.5423	16.8
22	1.987	19.5	82.62	66.1	84.92	0.8331	22.5
23	2.270	22.3	77.21	61.8	92.63	0.9087	21.1
24	1.867	18.3	60.59	48.5	51.07	0.5010	16.5
25	2.020	19.8	73.91	59.1	80.97	0.7943	20.2
26	1.958	19.2	62.53	50.0	58.94	0.5782	17.1
27	2.148	21.1	75.54	60.4	90.55	0.8883	20.6
28	2.234	21.9	72.70	58.2	83.48	0.8189	19.8
29	1.929	18.9	62.83	50.3	62.23	0.6105	17.1
30	1.985	19.5	67.83	54.3	69.99	0.6866	18.5
MEAN	2.07	20.3	71.6	57.3	76.4	0.7491	19.5
Std Dev	0.188	1.848	6.191	4.954	13.570	0.1331	1.687

*Note: Nm = kgf mm/A x 0.00981

Sample: 60 freeze-thaw - wet

Gauge Length: 125 mm
TestSpeed: 220 mm/60s
Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	1.974	19.4	66.54	53.2	65.90	0.6465	18.1
2	2.400	23.5	84.46	67.6	102.8	1.0085	23.0
3	2.158	21.2	74.49	59.6	78.76	0.7726	20.3
4	2.303	22.6	85.41	68.3	108.2	1.0614	23.3
5	1.915	18.8	65.44	52.4	65.65	0.6440	17.8
6	2.472	24.3	88.35	70.7	122.0	1.1968	24.1
7	1.897	18.6	74.44	59.6	75.88	0.7444	20.3
8	2.098	20.6	67.78	54.2	71.26	0.6991	18.5
9	2.475	24.3	80.07	64.1	101.1	0.9918	21.8
10	1.689	16.6	58.72	47.0	46.70	0.4581	16.0
11	1.793	17.6	66.93	53.5	61.63	0.6046	18.3
12	2.345	23.0	69.34	55.5	87.13	0.8547	18.9
13	1.875	18.4	71.38	57.1	66.63	0.6536	19.5
14	2.332	22.9	74.56	59.6	98.58	0.9671	20.3
15	2.201	21.6	74.44	59.6	83.84	0.8225	20.3
16	2.085	20.5	78.93	63.1	93.19	0.9142	21.5
17	2.144	21.0	72.13	57.7	85.07	0.8345	19.7
18	1.860	18.2	74.52	59.6	79.11	0.7761	20.3
19	2.130	20.9	69.78	55.8	81.83	0.8028	19.0
20	1.965	19.3	79.22	63.4	80.34	0.7881	21.6
21	1.776	17.4	74.60	59.7	72.53	0.7115	20.3
22	1.907	18.7	72.03	57.6	71.02	0.6967	19.6
23	2.070	20.3	70.56	56.4	80.48	0.7895	19.2
24	2.494	24.5	75.34	60.3	99.25	0.9736	20.5
25	2.038	20.0	78.11	62.5	83.24	0.8166	21.3
26	2.000	19.6	68.21	54.6	66.08	0.6482	18.6
27	2.044	20.1	64.18	51.3	71.72	0.7036	17.5
28	2.035	20.0	68.33	54.7	77.66	0.7618	18.6
29	2.325	22.8	80.43	64.3	101.9	0.9996	21.9
30	2.263	22.2	79.03	63.2	89.44	0.8774	21.6
MEAN	2.10	20.6	73.6	58.9	82.3	0.8073	20.1
Std Dev	0.221	2.173	6.681	5.347	16.038	0.1573	1.823

*Note: Nm = kgf mm/A x 0.00981

Tensile Raw Data (cont.)

Sample: 60 days - continuous freeze - dry

Gauge Length: 125 mm
TestSpeed 220 mm/60s

Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	2.283	22.4	78.66	62.9	96.45	0.9462	21.5
2	2.412	23.7	76.37	61.1	102.2	1.0026	20.8
3	2.055	20.2	68.66	54.9	71.39	0.7003	18.7
4	2.032	19.9	67.71	54.2	64.90	0.6367	18.5
5	1.933	19.0	60.77	48.6	54.01	0.5298	16.6
6	2.091	20.5	75.95	60.8	74.74	0.7332	20.7
7	2.231	21.9	72.95	58.4	86.23	0.8459	19.9
8	2.200	21.6	67.59	54.1	81.61	0.8006	18.4
9	2.235	21.9	78.19	62.6	95.81	0.9399	21.3
10	2.072	20.3	71.33	57.1	83.36	0.8178	19.5
11	1.797	17.6	63.63	50.9	53.83	0.5281	17.4
12	2.075	20.4	64.95	52.0	73.51	0.7211	17.7
13	1.848	18.1	74.30	59.4	66.60	0.6533	20.3
14	2.197	21.6	71.69	57.4	79.13	0.7763	19.6
15	2.105	20.7	68.76	55.0	76.24	0.7479	18.8
16	2.036	20.0	80.04	64.0	82.94	0.8136	21.8
17	2.256	22.1	74.37	59.5	89.17	0.8748	20.3
18	2.142	21.0	75.60	60.5	82.15	0.8059	20.6
19	2.021	19.8	68.56	54.8	71.81	0.7045	18.7
20	2.396	23.5	71.70	57.4	89.00	0.8731	19.6
21	2.246	22.0	88.12	70.5	104.6	1.0261	24.0
22	1.828	17.9	71.23	57.0	63.31	0.6211	19.4
23	2.340	23.0	79.00	63.2	92.17	0.9042	21.5
24	2.313	22.7	75.95	60.8	88.15	0.8648	20.7
25	2.356	23.1	77.27	61.8	94.26	0.9247	21.1
26	2.030	19.9	67.62	54.1	71.39	0.7003	18.4
27	2.117	20.8	66.82	53.5	61.19	0.6003	18.2
28	1.811	17.8	57.18	45.7	48.94	0.4801	15.6
29	2.166	21.2	67.63	54.1	73.74	0.7234	18.4
30	2.421	23.8	80.61	64.5	107.9	1.0585	22.0
MEAN	2.13	20.9	72.1	57.7	79.4	0.7785	19.7
Std Dev	0.179	1.759	6.528	5.226	15.243	0.1495	1.775

*Note: Nm = kgf mm/A x 0.00981

Sample: 60 days - continuous freeze - wet

Gauge Length: 125 mm
TestSpeed 220 mm/60s

Load Range: 0-5 kgf

Specimen	Peak Load (kgf)	Peak Load (N)	Elongation (mm)	Extension (%)	Energy (kgf mm/A)	Energy *(Nm or J)	Break Time (s)
1	2.532	24.8	84.43	67.5	113.7	1.1154	23.0
2	1.949	19.1	77.38	61.9	71.21	0.6986	21.1
3	2.101	20.6	72.79	58.2	79.88	0.7836	19.9
4	2.079	20.4	76.68	61.3	88.02	0.8635	20.9
5	2.034	20.0	77.32	61.9	78.17	0.7668	21.1
6	2.197	21.6	79.93	63.9	98.01	0.9615	21.8
7	1.964	19.3	86.24	69.0	81.73	0.8018	23.5
8	1.991	19.5	72.62	58.1	72.86	0.7148	19.8
9	2.294	22.5	79.54	63.6	95.37	0.9356	21.7
10	2.027	19.9	76.05	60.8	81.78	0.8023	20.7
11	2.005	19.7	71.48	57.2	78.15	0.7667	19.5
12	2.091	20.5	71.79	57.4	80.98	0.7944	19.6
13	2.187	21.5	83.47	66.8	108.0	1.0595	22.8
14	2.593	25.4	83.48	66.8	122.0	1.1968	22.8
15	2.067	20.3	62.50	50.0	72.42	0.7104	17.0
16	2.047	20.1	70.77	56.6	79.63	0.7812	19.3
17	1.984	19.5	67.45	54.0	70.72	0.6938	18.4
18	2.105	20.7	74.16	59.3	78.59	0.7710	20.2
19	2.056	20.2	83.73	67.0	90.18	0.8847	22.8
20	2.060	20.2	72.36	57.9	82.45	0.8088	19.7
21	2.097	20.6	77.31	61.8	87.76	0.8609	21.1
22	2.298	22.5	76.28	61.0	100.2	0.9830	20.8
23	2.036	20.0	67.92	54.3	72.46	0.7108	18.5
24	2.294	22.5	82.91	66.3	94.95	0.9315	22.6
25	1.753	17.2	63.01	50.4	49.47	0.4853	17.2
26	2.087	20.5	83.95	67.2	84.90	0.8329	22.9
27	2.101	20.6	68.84	55.1	69.35	0.6803	18.8
28	2.177	21.4	73.46	58.8	77.55	0.7608	20.0
29	2.235	21.9	74.78	59.8	88.57	0.8689	20.4
30	2.181	21.4	77.49	62.0	88.17	0.8649	21.1
MEAN	2.12	20.8	75.7	60.5	84.6	0.8297	20.6
Std Dev	0.166	1.615	6.280	5.024	14.435	0.1416	1.714

*Note: Nm = kgf mm/A x 0.00981

Moisture Regain Raw Data

Sample: No freeze-dry

Specimen:	11%	32%	53%	65%	75%	97%
1	3.52	7.69	11.26	13.82	16.14	28.57
2	3.65	7.72	11.32	13.79	16.00	28.46
3	3.46	7.59	11.49	13.73	15.96	28.34
Mean R%	3.54	7.67	11.36	13.78	16.03	28.46
Std Dev.	0.097	0.068	0.119	0.046	0.095	0.115

Sample: No freeze - wet

Specimen:	11%	32%	53%	65%	75%	97%
1	3.33	7.58	11.39	13.74	16.09	29.13
2	3.29	7.59	11.28	13.85	15.93	28.29
3	3.28	7.58	11.27	13.68	15.98	28.78
Mean R%	3.30	7.58	11.31	13.76	16.00	28.73
Std Dev.	0.026	0.006	0.067	0.086	0.082	0.422

Sample: 20 cycles - freeze-thaw - dry

Specimen:	11%	32%	53%	65%	75%	97%
1	3.55	7.27	11.25	13.25	15.76	30.80
2	3.58	7.26	11.15	13.20	15.71	29.14
3	3.58	7.21	11.08	13.08	15.65	29.34
Mean R%	3.57	7.25	11.16	13.18	15.71	29.76
Std Dev.	0.017	0.032	0.085	0.087	0.055	0.906

Sample: 20 cycles - freeze-thaw - wet

Specimen:	11%	32%	53%	65%	75%	97%
1	3.42	7.51	10.88	13.34	16.13	28.88
2	3.36	7.58	10.78	13.27	16.03	29.65
3	3.49	7.38	10.62	13.13	15.83	29.34
Mean R%	3.42	7.49	10.76	13.25	16.00	29.29
Std Dev.	0.065	0.101	0.131	0.107	0.153	0.387

Sample: 20 days - continuous freeze - dry

Specimen:	11%	32%	53%	65%	75%	97%
1	3.19	7.40	11.08	13.40	16.08	28.74
2	3.06	7.59	11.09	13.25	15.88	28.88
3	3.18	7.42	10.91	13.13	15.76	29.39
Mean R%	3.14	7.47	11.03	13.26	15.91	29.00
Std Dev.	0.072	0.104	0.101	0.135	0.162	0.342

Regain Raw Data (cont.)

Sample: 20 days - continuous freeze - wet

Specimen:	11%	32%	53%	65%	75%	97%
1	3.33	7.27	11.09	13.65	15.96	29.20
2	3.00	7.30	10.88	13.59	15.93	29.54
3	3.22	7.29	10.72	13.46	15.79	28.36
Mean R%	3.18	7.29	10.90	13.57	15.89	29.03
Std Dev.	0.168	0.015	0.186	0.097	0.091	0.607

Sample: 40 cycles - freeze/thaw - dry

Specimen:	11%	32%	53%	65%	75%	97%
1	3.59	7.43	11.17	13.42	15.82	29.94
2	3.54	7.44	11.26	13.27	15.79	29.90
3	3.56	7.38	11.10	13.22	15.63	29.24
Mean R%	3.56	7.42	11.18	13.30	15.75	29.69
Std Dev.	0.025	0.032	0.080	0.104	0.102	0.393

Sample: 40 cycles - freeze/thaw - wet

Specimen:	11%	32%	53%	65%	75%	97%
1	3.13	7.37	11.21	13.59	16.00	28.92
2	3.07	7.41	11.12	13.46	15.82	29.37
3	3.04	7.38	11.10	13.37	15.66	29.98
Mean R%	3.08	7.39	11.14	13.47	15.83	29.42
Std Dev.	0.046	0.021	0.059	0.111	0.170	0.532

Sample: 40 days - continuous freeze - dry

Specimen:	11%	32%	53%	65%	75%	97%
1	3.36	7.09	11.03	13.47	15.94	29.70
2	3.19	7.02	10.88	13.55	15.93	29.43
3	3.15	6.91	10.80	13.27	15.82	28.92
Mean R%	3.23	7.01	10.90	13.43	15.90	29.35
Std Dev.	0.112	0.091	0.117	0.144	0.067	0.396

Sample: 40 days - continuous freeze - wet

Specimen:	11%	32%	53%	65%	75%	97%
1	3.23	7.72	11.46	13.33	16.07	28.51
2	3.23	7.65	11.28	13.31	15.97	29.59
3	3.33	7.57	11.25	13.20	15.86	29.17
Mean R%	3.26	7.65	11.33	13.28	15.97	29.09
Std Dev.	0.058	0.075	0.114	0.070	0.105	0.544

Regain Raw Data (Cont.)

Sample: 60 cycles - freeze/thaw - dry

Specimen:	11%	32%	53%	65%	75%	97%
1	2.91	7.47	11.33	13.62	16.04	28.98
2	3.00	7.29	11.28	13.47	15.94	29.72
3	2.98	7.42	11.15	13.35	15.79	29.25
Mean R%	2.96	7.39	11.25	13.48	15.92	29.32
Std Dev.	0.047	0.093	0.093	0.135	0.126	0.374

Sample: 60 cycles - freeze/thaw - wet

Specimen:	11%	32%	53%	65%	75%	97%
1	3.17	7.58	11.38	13.56	16.07	29.58
2	3.18	7.64	11.11	13.41	15.86	29.76
3	3.02	7.63	10.92	13.16	15.77	30.03
Mean R%	3.12	7.62	11.14	13.38	15.90	29.79
Std Dev.	0.090	0.032	0.231	0.202	0.154	0.226

Sample: 60 days - continuous freeze - dry

Specimen:	11%	32%	53%	65%	75%	97%
1	3.49	7.72	11.31	14.07	16.57	30.04
2	3.47	7.75	10.97	14.01	16.36	29.46
3	3.44	7.70	10.87	13.83	16.34	29.24
Mean R%	3.47	7.72	11.05	13.97	16.42	29.58
Std Dev.	0.025	0.025	0.231	0.125	0.127	0.413

Sample: 60 days - continuous freeze - wet

Specimen:	11%	32%	53%	65%	75%	97%
1	3.69	8.18	11.75	13.44	15.92	29.83
2	3.77	8.12	11.79	13.32	15.80	29.89
3	3.89	8.18	11.70	13.19	15.77	30.33
Mean R%	3.78	8.16	11.75	13.32	15.83	30.02
Std Dev.	0.101	0.035	0.045	0.125	0.079	0.273

BET Monolayer Value (M1) Raw Data

Specimen:	No Freeze-dry	No Freeze-wet
1	5.86	6.02
2	5.84	5.97
3	6.01	5.97
Mean R%	5.90	5.99
Std Dev.	0.093	0.029

Specimen:	20 FT-dry	20 FT-wet	20 Cont-dry	20 Cont-wet
1	5.80	5.66	5.88	5.80
2	5.73	5.63	5.98	5.85
3	5.68	5.46	5.78	5.63
Mean R%	5.74	5.58	5.88	5.76
Std Dev.	0.060	0.108	0.100	0.115

Specimen:	40 FT-dry	40-FT-wet	40 Cont-dry	40 Cont-wet
1	5.75	5.99	5.73	6.13
2	5.82	5.97	5.72	6.01
3	5.72	5.98	5.68	5.93
Mean R%	5.76	5.98	5.71	6.02
Std Dev.	0.051	0.010	0.026	0.101

Specimen:	60 FT-dry	60 FT-wet	60 Cont-dry	60 Cont-wet
1	6.22	6.10	5.90	6.12
2	6.11	5.93	5.71	6.10
3	6.05	5.90	5.66	6.01
Mean R%	6.13	5.98	5.76	6.08
Std Dev.	0.086	0.108	0.127	0.059

Tributylphosphine-Alcoholic Sodium Iodide Solubility Raw Data

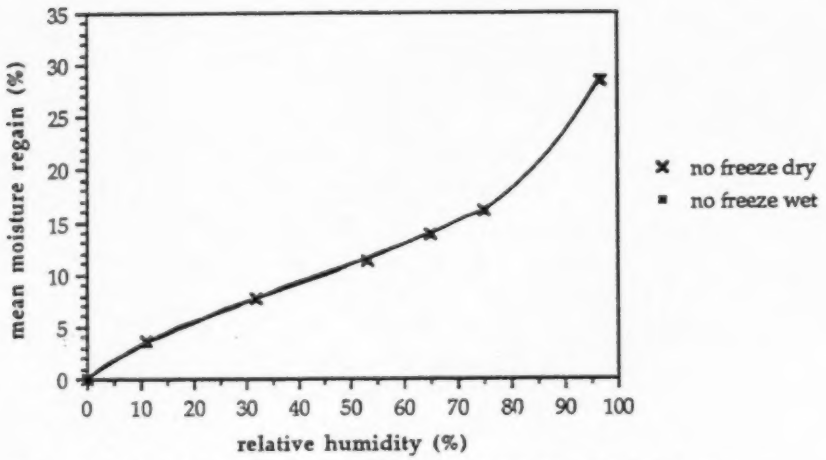
Specimen:	No Freeze-dry	No Freeze-wet
1	44.33	45.86
2	43.65	45.35
Mean S%	43.99	45.61
Std Dev.	0.481	0.361

Specimen:	20 FT-dry	20 FT-wet	20 Cont-dry	20 Cont-wet
1	44.86	43.01	43.16	44.32
2	44.80	43.09	42.33	44.59
Mean S%	44.83	43.05	42.75	44.46
Std Dev.	0.042	0.057	0.587	0.191

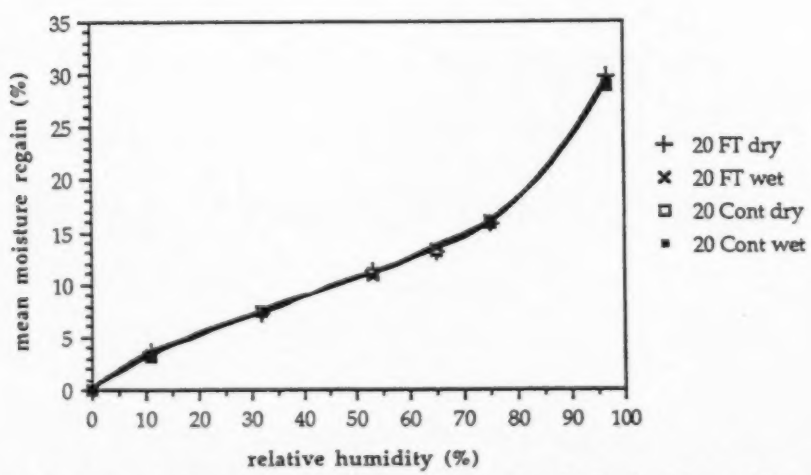
Specimen:	40 FT-dry	40 FT-wet	40 Cont-dry	40 Cont-wet
1	43.94	44.05	43.17	42.64
2	44.90	44.33	43.40	43.60
Mean S%	44.42	44.19	43.29	43.12
Std Dev.	0.679	0.198	0.163	0.679

Specimen:	60 FT-dry	60 FT-wet	60 Cont-dry	60 Cont-wet
1	43.22	42.68	43.39	43.02
2	43.97	41.67	43.96	43.03
Mean R%	43.60	42.18	43.68	43.03
Std Dev.	0.530	0.714	0.403	0.007

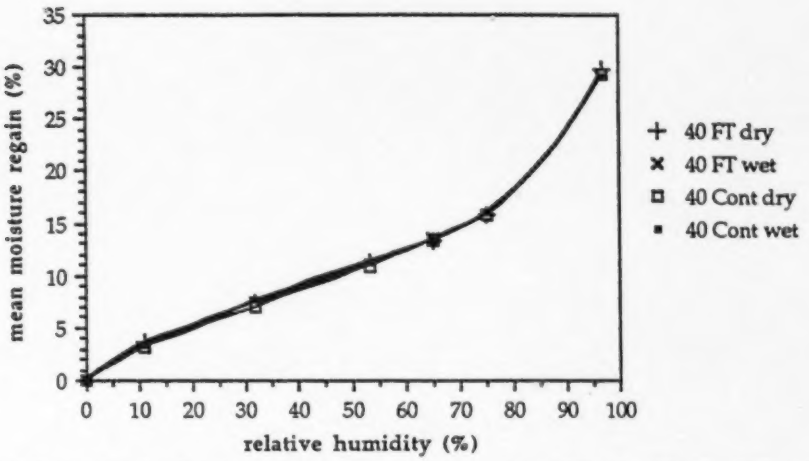
APPENDIX A-4: Moisture Sorption Isotherms



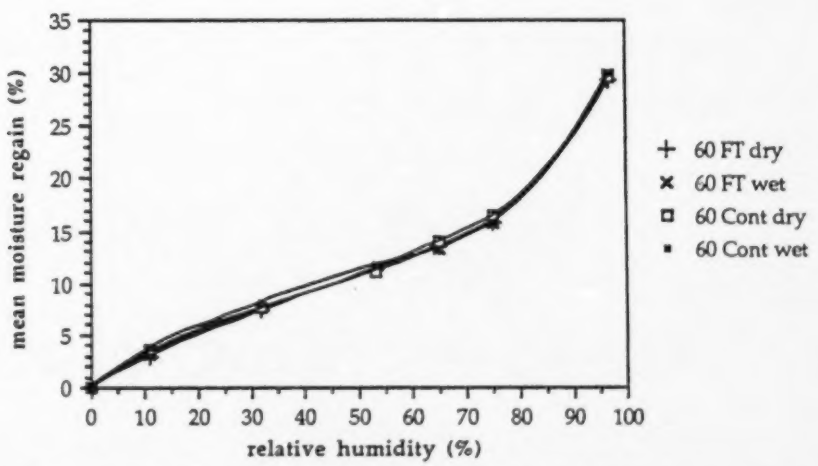
Moisture Adsorption Isotherms for Wool Yarns Which Had Not Been Frozen



Moisture Adsorption Isotherms for Wool Yarns Exposed to 20 Cycles/Days of Freezing



Moisture Adsorption Isotherms for Wool Yarns Exposed to 40 Cycles/Days of Freezing



Moisture Adsorption Isotherms for Wool Yarns Exposed to 60 Cycles/Days of Freezing